In-depth Practical Course, 2004 SS Semester

Measurements of Heats of Adsorption with a Tian-Calvet Microcalorimeter

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1 Principles

1.1 Differential heat of adsorption

The measurement of the heat of adsorption by a suitable microcalorimeter is the most reliable method to study the strength of interaction between adsorbed species and adsorbents. There are different definitions of heats of adsorption, which are measured under different circumstance; a Tian-Calvet microcalorimeter measures the differential heat of adsorption.

The differential heat of adsorption (q^{diff}) is a change in internal energy, it is related to the integral heat of adsorption (Q^{int}) according to

$$q^{\mathrm{diff}} = \left\{ \frac{\partial Q^{\mathrm{int}}}{\partial n^{\sigma}} \right\}_{T,m,V^{\mathrm{g}}} \tag{1.1}$$

where the superscript σ refers to the Gibbs surface, i.e. a surface up to which both the gas phase and the solid are assumed to be homogeneous[1]. The integral heat of adsorption (Q^{int}) is defined as the amount of heat evolved by system when a certain amount of adsorbtive n^{σ} are adsorbed at constant temperature and volume[1]:

$$-Q^{\mathrm{int}} = n^{\sigma}(u^{\sigma} - u^{\mathrm{g}}) \tag{1.2}$$

The differential heat of adsorption can be measured fairly accurately in an adsorption experiment if the "step width" (Δn^{a}) is small enough.

1.2 Tian-Calvet Microcalorimeter

A Tian-Calvet microcalorimeter is a kind of differential scanning calorimeter (DSC). As all other DSCs, its measuring system has a twin-type design of same kind, so that the disturbance such as temperature variation in the environment of the measuring system, expansion of adsorbtive gas and so on will affect the two measuring systems in the same way, and are compensated when the difference between the individual signals is formed. Besides, the difference signal can be strongly amplified, because the high basic signal is almost compensated by the reference system.

The Tian-Calvet microcalorimeter belongs to heat flux DSCs. In heat flux DSCs, a defined exchange of the heat to be measured with the environment takes place via a well-defined heat conduction path with given thermal resistance. The primary measurement signal is a temperature difference, which determines the intensity of exchange; and the flow rate Φ can be calculated out from it[2].

In more detail, a Tian-Calvet microcalorimeter belongs to the type of heat flux DSCs with cylindrical measuring system. A block-type cylindrical furnace is provided with two cylindrical cavities, each containing a cylindrical, fixed cell which is connected with the furnace (or directly with the other cell) by means of thermopiles (Fig. 1.1). The outer surface of each cell is in contact with a great number of thermocouples connected in series between the container and the furnace. Both cells are thermally decoupled; heat exchange takes place only with part of the massive furnace.

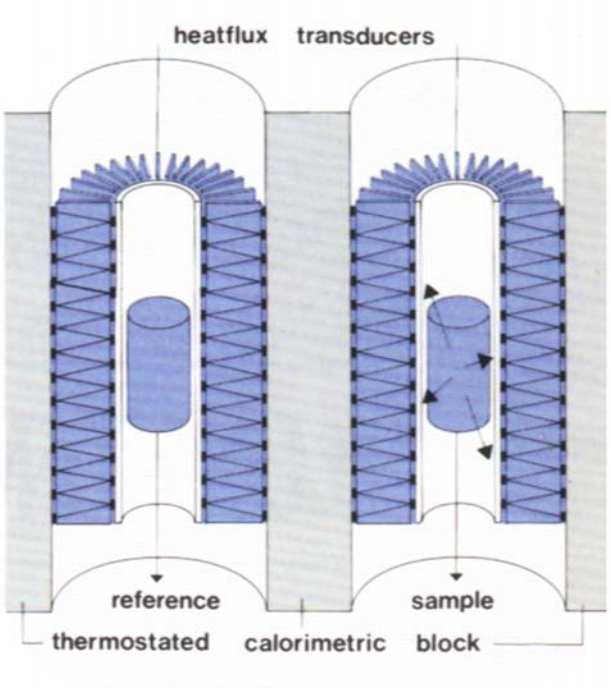

Fig. 1.1 Heat flux DSC with cylinder-type system[2]

The measurement signal proper of a heat flux DSC is the temperature difference ΔT of both cells averaged over surface; it is generated by differential connection of both thermopiles:

$$\Delta T = \Delta T_{FS} - \Delta T_{FR} = \Delta T_{SR} \tag{1.3}$$

The heat flow rate $\Phi_r(t)$can be obtained from the change of $\Delta T(t)$ with Tian's equation [2]:

$$\Phi_r(t) = -\frac{\Delta T(t)}{R} - (C_S - C_R)\cdot\beta - \frac{\tau}{R}\cdot\frac{d\Delta T(t)}{dt} \tag{1.4}$$

Where R is the global heat resistance between the furnace and the cells (the cells should be thermal symmetry), C_S and C_R are the heat capacity of sample and reference, β is the heating rate, τ is a time constant and equals to $C_S R$.

For a measurement of heat of adsorption, the heating rate is often zero (i.e. isothermal), so

$$\Phi_r(t) = -\frac{\Delta T(t)}{R} - \frac{\tau}{R} \cdot \frac{d\Delta T(t)}{dt} \tag{1.4}$$

Since the τ and R are calorimeter constants, the $\Delta T(t)$ can be measured out by the thermopile, thus $\Phi_r(t)$ can be calculated out every time. The interval heat of adsorption can be obtained by calculating the peak areas of measured curve

$$Q_r = \int \Phi_r \, dt \tag{1.5}$$

with the increasing amount of adsorbates, the differential heats of adsorption can be calculated out.

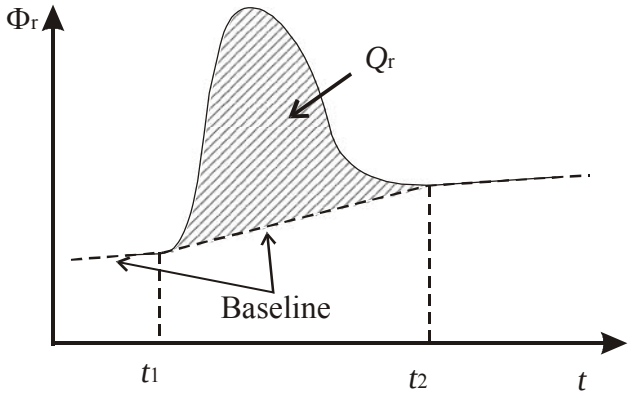

Fig 1.2 Getting Q_r from measured Φ_r -t curve

2 Setup

The system for measuring heat of adsorptions has a Tian-Calvet microcalorimeter and the auxiliary parts, including gas supplying unit, temperature and pressure control units. It is modified after the setup by Spiewak and Dumesic[3]. All the gas lines, including tubes, valves and connections, are metal wares so that a ultra high vacuum can be obtained.

2.1 Connection fittings

Connection fittings are very important in a vacuum system, because they are necessary to combine different parts and have the most significant influence on the tightness of the system. There are three kinds of connection fittings applied in the system, SWAGELOK fittings, SWAGELOK CAJON VCR fittings, and CF flanges. A KF flange is used in the connection of a rough vacuum pump.

2.1.1 SWAGELOK tube fittings and adapter fittings[4]

SWAGELOK tube fittings are used to combine gas tubes (two types of metal tubes are applied as gas line, one is 1/4 inch and the other is 1/8 inch). They includes different shapes: unions and connectors in straight or elbow configurations. A typical SWAGELOK fitting has one nut and two ferrules.

Fig 2.1 shows its working mechanism: The elements of the fitting are depicted in cross-section prior to make-up: the fitting nut (top), the advanced geometry back ferrule (left), the front ferrule (center), and the fitting body (right). The tube wall section is shown below the ferrules and body. During make-up, the front ferrule (center) is driven into the body of the fitting (right) and the tube (bottom) to create primary seals (tube and body), while the back ferrule (left) hinges inward to create a strong grip on the tube.

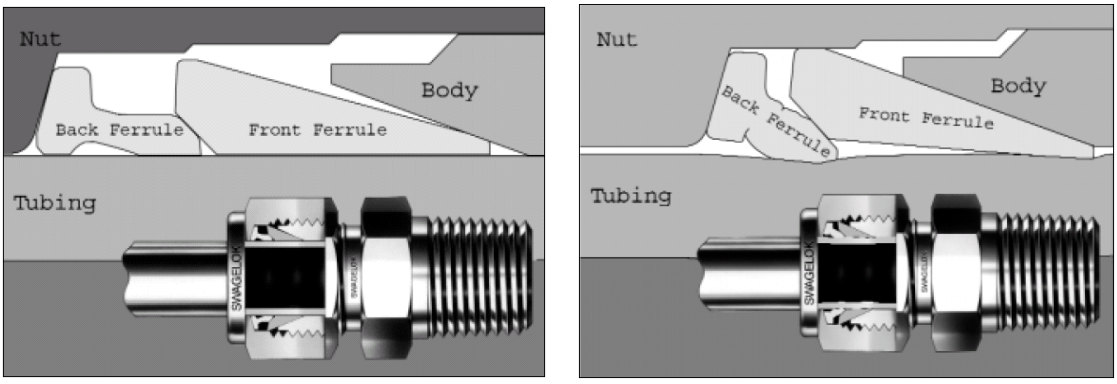

Fig. 2.1 SWAGELOK tube fitting

Left: 316 SS Advanced SWAGELOK Tube Fitting prior to make-up; right: after Make-up

A SWAGELOK tube fitting can be reusable until the edge of the front ferrule nearly reaches the edge of the back ferrule. If that happens, cut a small segment of the tube with the ferrules and use a pair of new ferrules.

It should be noticed that there are two specifications of SWAGELOK tube fittings, one is metric and the other is in length based on inches; they cannot interchange. All metric tube fittings have a stepped shoulder on the body hex. Shaped fittings, such as elbows, crosses, and tees, are stamped MM for metric tubing, and have no step on forging (Fig. 2.2).

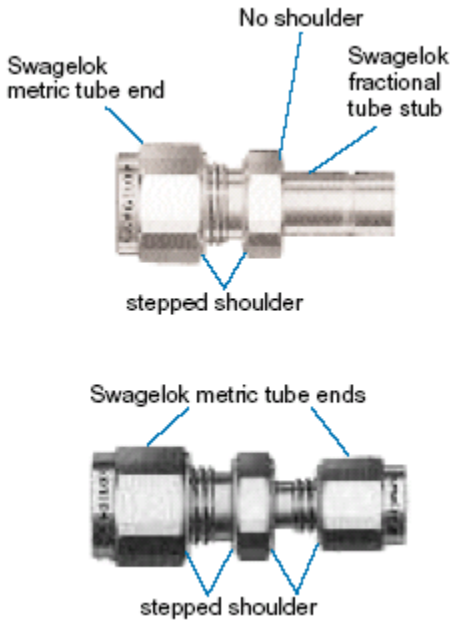

Fig 2.2 Distinguishing a SWAGELOK metric fitting

To install a new SWAGELOK tube fitting in this system (larger than 1 in. / 25 mm), insert tubing into the SWAGELOK tube fitting, make sure that the tubing rests firmly on the shoulder of the tube fitting body and that the nut is finger-tight. Then scribing the nut at the 6 o'clock position. While holding fitting body steady, tighten the nut 1 1/4 turns to the 9 o'clock position (Fig 2.3).

Fig 2.3 Installation of a SWAGELOK tube fittin SWAGELOK tube fitting

If a SWAGELOK tube fitting was used before, just tighten it for 1/2 turn.

2.1.2 SWAGELOK CAJON VCR connection[5]

A whole set of SWAGELOK CAJON VCR connection includes two glands and two nuts; or includes a female nut, a body part and a gland (Fig 2.4) . They can also be connected to SWAGELOK or PFEIFFER valves, and the sensors of MKS Baratron pressure transducers. In this setup all connections of this type are made of stainless steel. The surface of the glands is polished very finely; if the it is damaged, thread galling may occur, which will damage the fitting components cause a poor seal. So they cannot be cleaned with chemicals, and cannot be touched by hand.

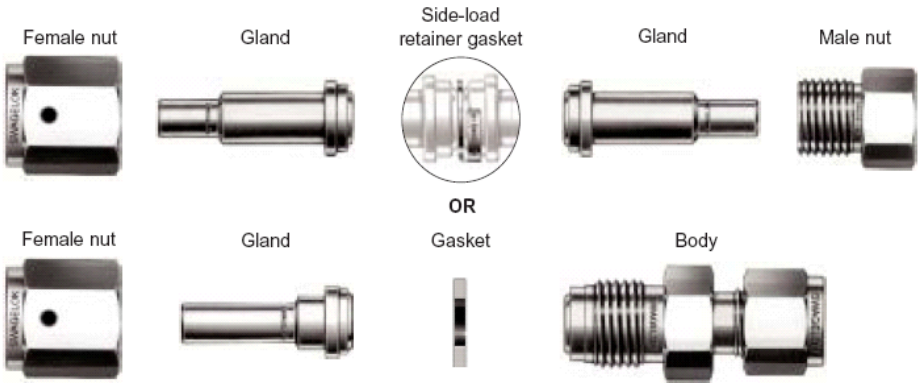

Fig 2.4 SWAGELOK CAJON VCR connection

There are two kinds of gaskets used for the VCR connection (Fig 2.5):

1. non-retained style

The size is 5.6mm for inner diameter (E), 11.9mm for outer diameter (Tx), and 0.7mm for thickness (H). There are two types for this style, one is silver plated, the ordering number of which is SS-4-VCR-2; the other is unplated, its number is SS-4-VCR-2-VS. The former one is softer and the latter one is harder. For a VCR connection which is disconnected and connected frequently, the former type should be used to avoid the damage on the surface of VCR bodies and glands.

2. Gasket retainer assembly

The Retainer and gasket must be used as an assembly. the size is 6.1mm for inner diameter (E), 12.7mm for outer diameter (Tx), and 0.7mm for thickness (H) There are also two types, Number SS-4-VCR-2-GR is plated and Number SS-4-VCR-2-GR-VS is unplated.

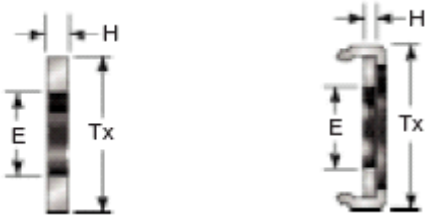

Fig 2.5 Gasket for SWAGELOK CAJON VCR connection: non retained style (left) and Gasket retainer assembly (right)

The installation instruction of a SWAGELOK CAJON VCR connection is shown in Fig 2.6. First, tighten the different fittings and a suitable gasket with finger(the surface of a gasket can not be touched by hand, otherwise it will be contaminated and cause a poor tightness), then use two wrenches, turn 45° to make tight.

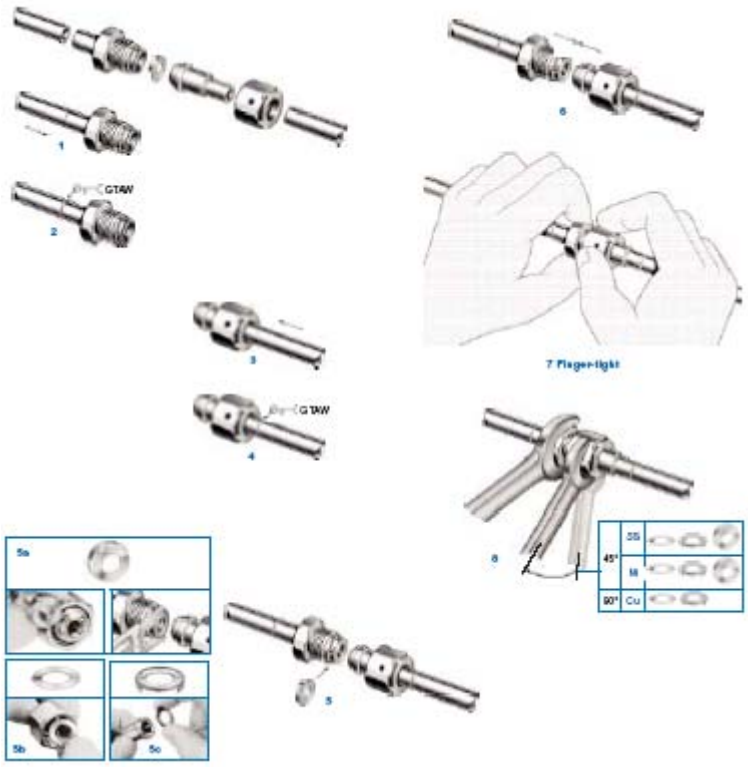

Fig 2.6 VCR Fitting Installation Instructions

The highest temperature for the SWAGELOK CAJON VCR stainless fittings and gaskets is 537°C (1000°F). The maximum leak rate for helium tested by the cooperation is $4x10^{-9}$ std cm^3/s for a connection with silver-plated gaskets and 4×10^{-11} std cm^3/s with unplated gaskets.

A VCR connection is easy to install and disassemble; but if it is too frequently, its tightness will get worse.

2.1.3 CF Flange

CF flanges are used for the frequent install and disassembling position, i. e. the connection between the sample cell and the T-piece, between the reference cell and the T-piece in the measuring cell (see section 2.2.5); and the connection to connect the measuring cell with other parts of the setup. It is also used in the cap of a chamber for calibration, the volume of which should be kept constant (see section 3.4).

To install a CF flange, place an OFE(oxygen-free electronic grade) copper gasket against the knife edge seal of one of two standard CF flanges, preferably the flange most likely to hold and support

the gasket from falling. With the gasket in place arrange mating flange with the desired bolt hole orientation. After hand tightening all bolts, support bolt and turn nut. The tightening process must be done gradually in 1/4 to 1/2 turn increments in a alternating crisscross pattern. Continue until the desired torque ratings have been achieved. Tightening bolts in this fashion will insure a reliable seal with even gasket compression and deformation[6].

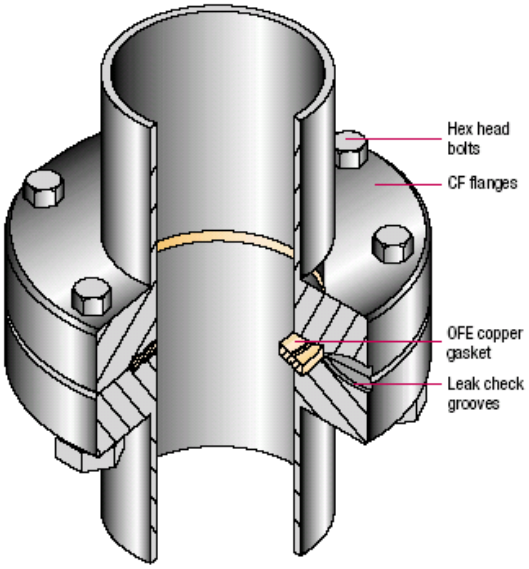

Fig 2.7 Structure of a CF flange[6]

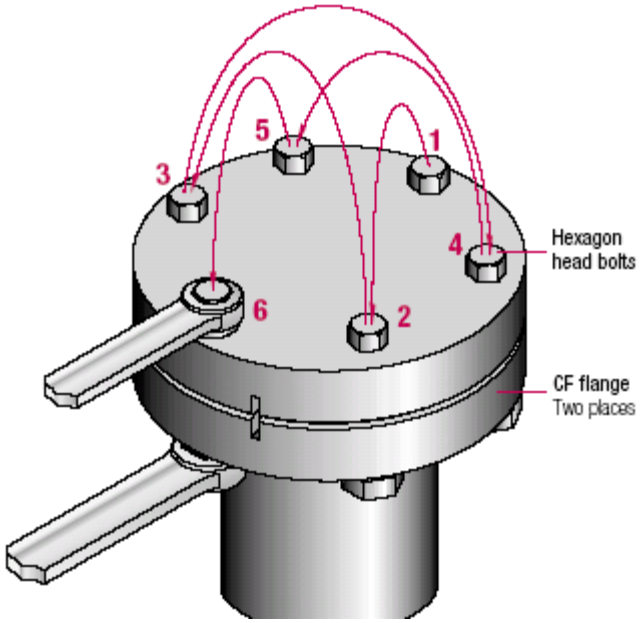

Fig 2.8 CF flange Installation[6]

The vacuum range for a CF flange can be as low as $1x10^{-11}$ Pa. The temperature range for CF flange is -200°C to 450°C. Besides, it can be opened and closed for over 5000 times with a good feature for vacuum.

2.1.4 KF Flange

A KF flange is applied to connect the rough vacuum pump to the system. Its most important advantage is that it can be connected and disconnected quickly. It uses a Viton O-ring, which can keep a vacuum of $1x10^{-4}$ Pa. This value is enough for the rough vacuum pump, because the latter can reach a vacuum of not lower than 10^{-2} Pa.

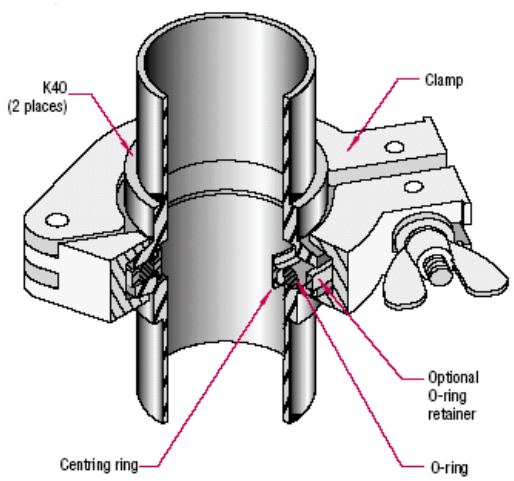

Fig 2.9 a KF flange[7]

2.2 Setup

The whole construction of the setup is shown as Fig 2.10 and Fig 2.11.

2.2.1 Gas Supplying

CO is applied as the adsorbtive gas and helium as the gas to calibrate volumes and to control the pressure in the system. The 50 L CO bottle (1) stands in the cabinet (Schrank 8) in the room (Fig 2.11), the 50L helium bottle (2) stands near the back of the computers. The purity of CO is 99.997% and the purity of helium is 99.99990%. Each kind of gas from the bottle goes through a pressure reducing valve with a pressure gauge (3, 4 and 5, 6), the pressure reducing gauges should be adjusted so that the relative pressure shown in the gauge is about 0 bar (i.e. the absolute pressure is 1 bar). The gases that reach the dosing section (the gas line between valve 18, 19 and 20) can be switched by shut-off valve 7 and 8. Before the gases comes to the pneumatic valve 20, they should pass through a filter (9) to avoid the damage of the pneumatic valve by dusts.

The gas pressure inside either bottle should be over 10 bar; if the pressure is lower than that, the gas bottle should be substituted.

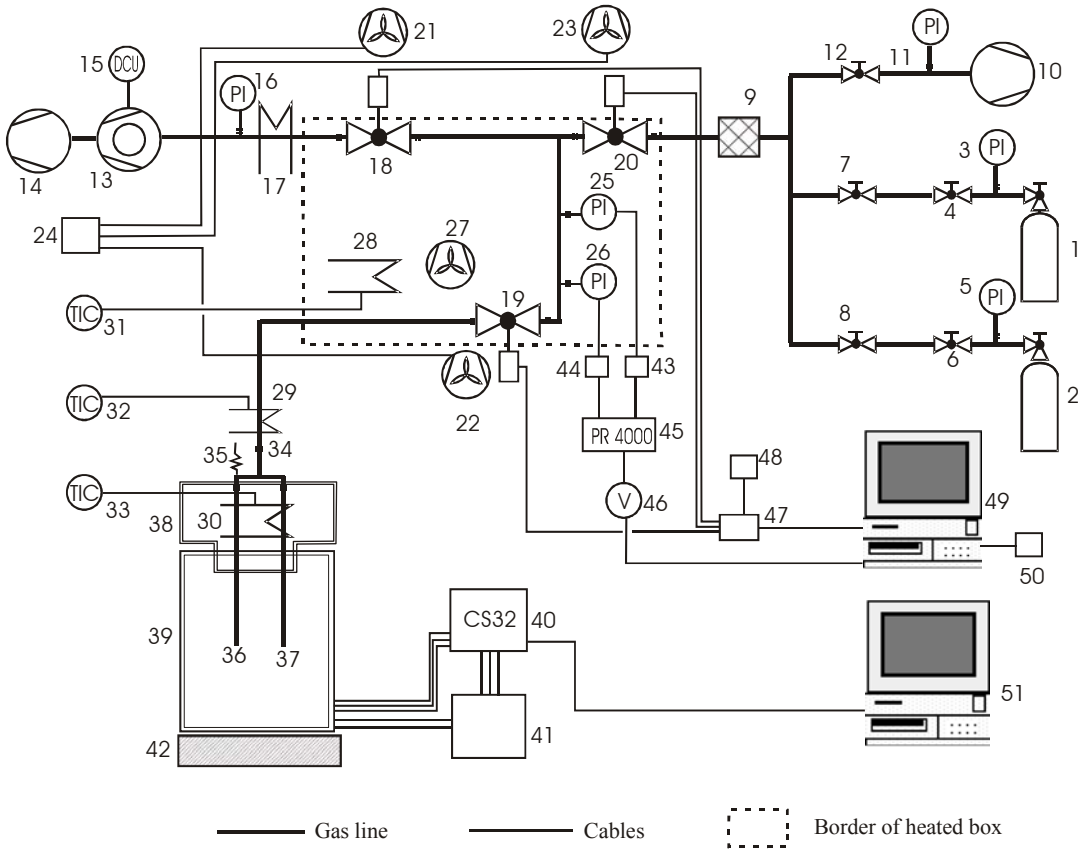

Fig 2.10 Setup

1 – CO bottle;
2 – helium bottle;
3 – CO supplying pressure gauge;
4 – CO pressure reducing valve;
5 – helium supplying pressure gauge;
6 – helium pressure reducing valve;
7 – shut–off valve for CO;
8 – shut–off valve for helium;
9 – filter;
10 – rough vacuum pump;
11 – Pirani gauge;
12 – shut–off valve for rough vacuum;
13 – turbopump;
14 – mechanic pump;
15 – Digital control unit of turbo pump 13
16 – full range pressure gauge;
17 – heater for the gas line to the turbo pump;
18 – turbopump valve;
19 – calorimeter valve;
20 – gas–supply valve;
21 – fan for the solenoid valve controlling the turbopump valve 18;
22 – fan for the solenoid valve controlling the calorimeter valve 19;
23 – fan for the solenoid valve controlling the gas–supply valve 20;
24 – Power supply for fans 21, 22, 23;
25 – Sensor for Baratron–1atm;
26 – Sensor for Baratron–100Pa;
27 – fan in heated box;
28 – oven heating the heated box;
29 – heating tape
30 – oven heating the auxiliary thermostat;
31 – temperature controller for oven 28;
32 – temperature controller for heating tape 29;
33 – temperature controller for the auxiliary thermostat 30;
34 – CF flange to connect measuring cell;
35 – Linear motion feedthrough with thread adapter;
36 – sample cell;
37 – reference cell;
38 – auxiliary thermostat;
39 – Calorimeter block;
40 – CS 32 controller for the calorimeter;
41 – Power module for the calorimeter;
42 – Linear adjust device for the calorimeter;
43 – Signal conditioner for Baratron-1atm;
44 – Signal conditioner for Baratron-100Pa;
45 – PR4000 power supply and readout;
46 – Voltmeter;
47 – Controller for the solenoid valves 18, 19, 20;
48 – Power supply for the solenoid valves 18, 19, 20;
49 – pressure and gas supplying controlling computer “Quincy”;
50 – Power failure protector;
51 – calorimeter controlling computer “Calvet”

Fig. 2. 11 Photos showing the position of the parts of the setup

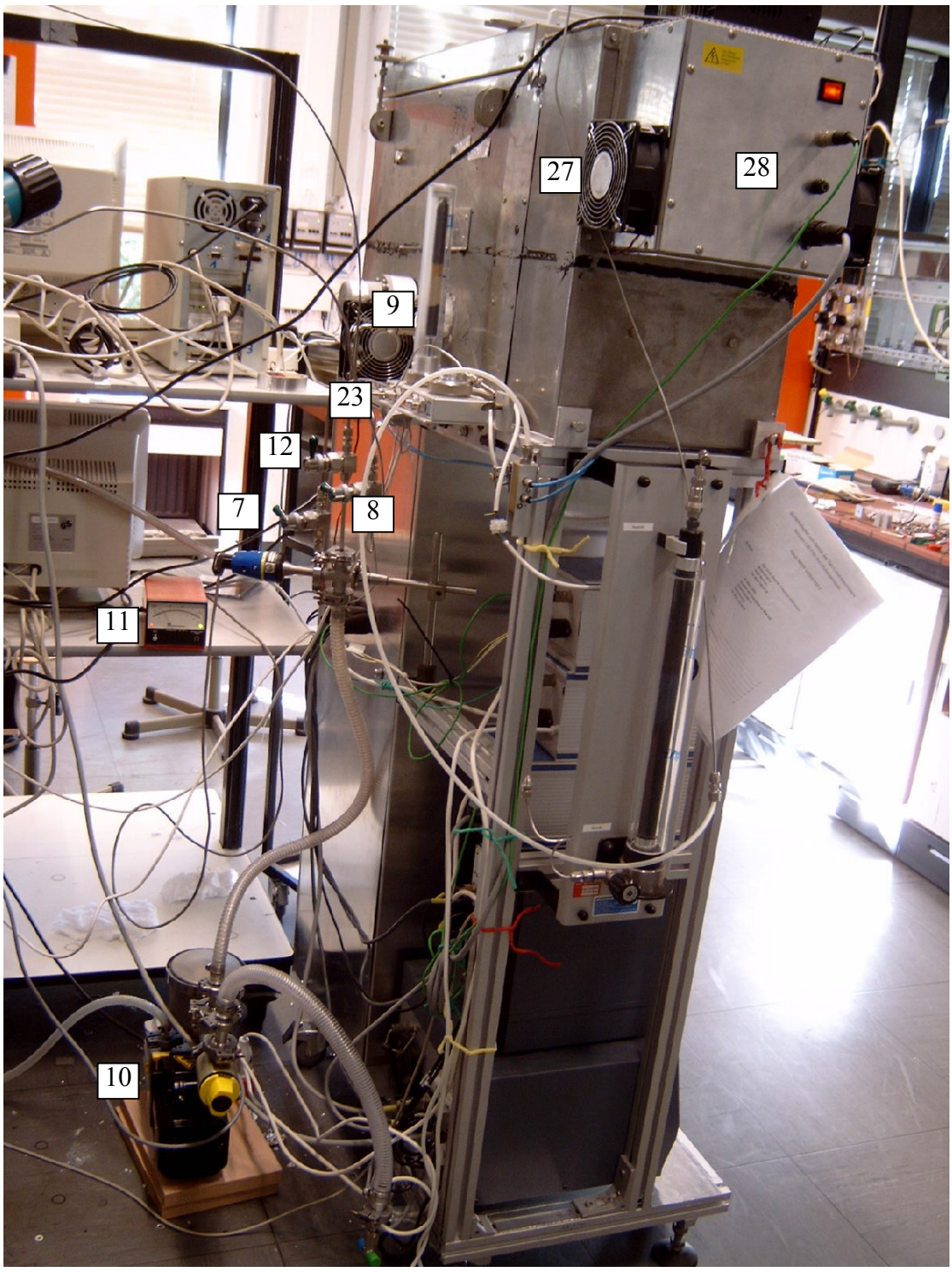

Fig. 2.11 (continued)

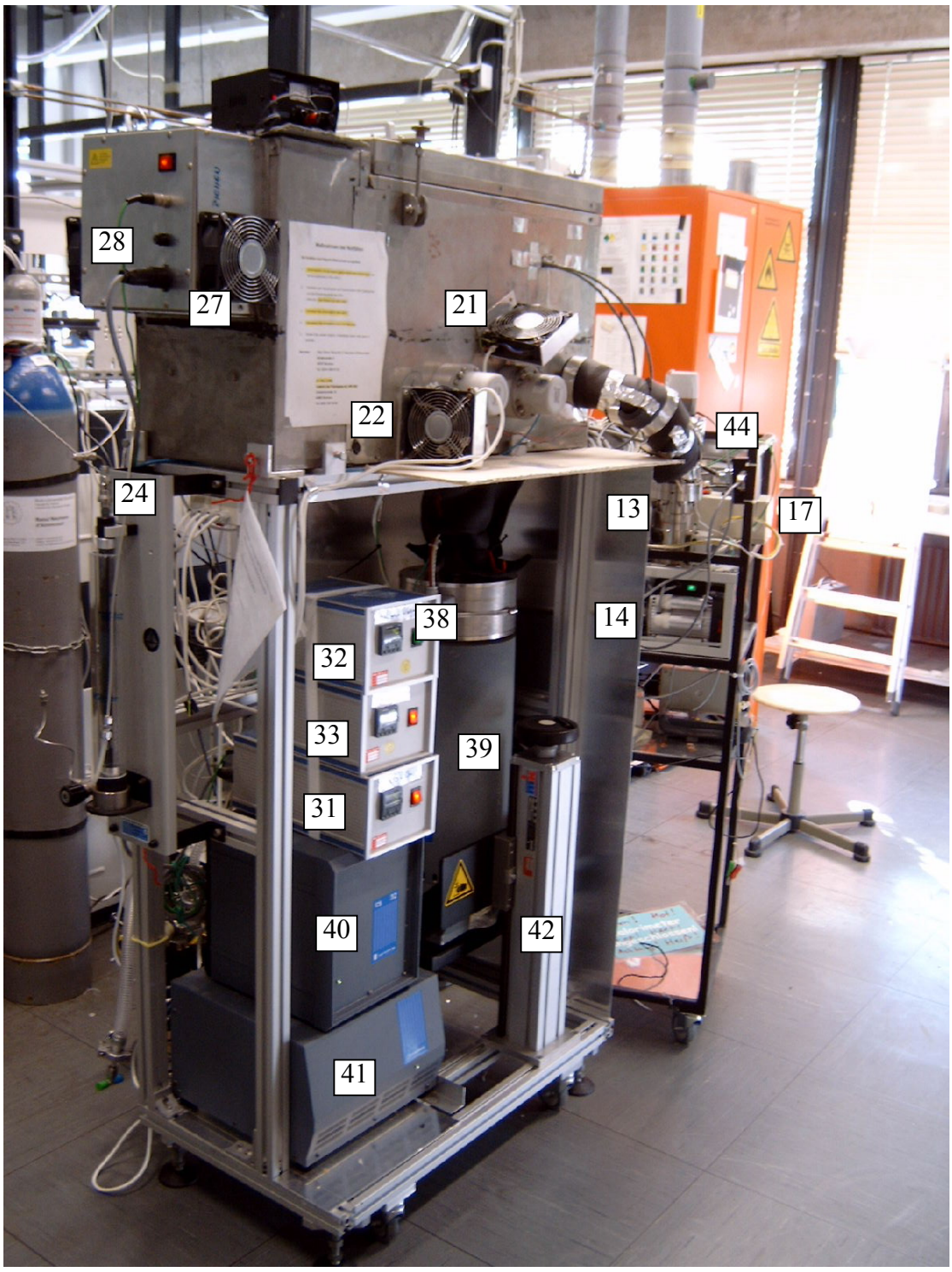

Fig. 2.11 (continued)

2.2.2 Pumps

The system uses a rough vacuum pump (10) to get a rough vacuum (1 bar – 1mbar), and a turbo pump (11) to get a ultra-high vacuum (< 10^{-7} mbar). The turbo pump should work with a mechanic pump (12) in series connection.

The rough vacuum pump is a Pfeiffer DUO 2.5 pump, its series number is PKD 41 702A. It connects to the system with a valve (12). The final pressure can reach 2-4 x 10^{-2} mbar. The pressure can be read from a Pirani gauge (13). This pump also serves for the preparation of the sample capsule (See section 3.6.2), so there is a switch to open another gas line(Fig 2.11).

Since the system use CO, which is a kind of toxic gas, so it should be sure that **the outlet of the rough vacuum pump is connected to the ventilating arrangement of the laboratory!** Besides, since the shutoff valve of this vacuum is neighbor to the shutoff valves of CO and helium bottle, so **whenever before open the shut-off valve for rough vacuum (12), both the shutoff valves of the gas bottles (7) and (8) should be closed!** Otherwise gas in the bottles will be evacuate away.

The turbo pump is a TMP 071P turbomolecular pump. It is compacted with a Pfeiffer TSU 071E PM051 668 S pump. The turbo pump can only work under a pressure of lower than 1kPa, so whenever before opening or pulsing the turbo pump valve (18), the pressure in the dosing section should be lower than that!

The turbo pump has a display control unit (DCU) (15), which can display the status of the pump. A full range pressure gauge (14) measures the pressure of the gas line near the turbo pump. A heater (17) is set to heat the gas line to the turbo pump to prevent condensation of water steam. Its temperature is set as 75°C, which is the maximum for the sensor of the full range pressure gauge (14).

The turbo pump should always be on; only when a power failure will happen or some error occurred with the pump then can it be switched off.

2.2.3 Pneumatic valves, dosing section and heated box

There are three pneumatic valves in the setup, which control the adsorption procedure directly: the turbopump valve (18), the calorimeter valve (19), and the gas-supply valve (20). The gas line between them acts as the dosing segment, that means, the adsorbate gas is pooled here before it goes to the sample cell where adsorption happens.

A pneumatic valve works with a solenoid valve and is controlled by the latter (Fig 2.12). When the solenoid valve receive a signal from the pressure-control computer "Quincy" (49), it can make the pneumatic valve open, close, or give a pulse (open a short time then close). The solenoid valve use helium to make the pulse of the pneumatic valve, that means, when the solenoid valve receives a signal for pulse, it give a pulse of helium itself, the helium gas open the pneumatic valve for a short time. The minimum pulse time can be 0.20 second, and it can be increased by a step of 0.05 second in the controlling program in the computer Quincy.

The helium through the solenoid valve comes from the central gas supplying system (ZGV), its pressure affects the pressure change of the dosing section during a pulse sensitively. It can be adjusted at the supplying valve of helium from ZGV; now its relative pressure is adjusted as about 5.9 bar.

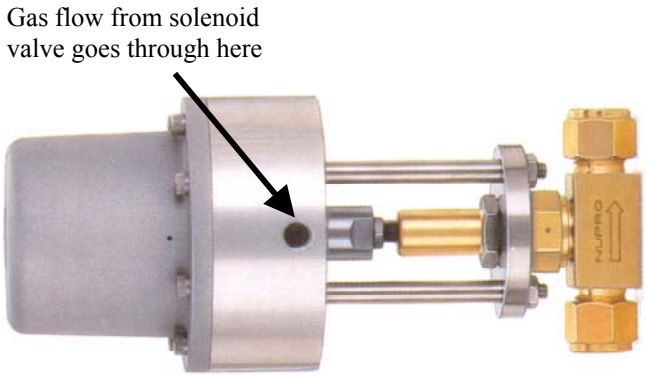

Fig 2.12 A pneumatic valve

To avoid the damage of pneumatic valves by dusts, besides the filter 9, one piece of SWAGELOK SS-4-VCR-2-2M gaskets, which can act as filters, is applied at each of the outside fittings of the turbopump valve and the calorimeter valve (i. e. the fittings between 18 and 16, and between 19 and 34 in Fig 2.10).

The dosing section is set in a heated box, where the temperature can reach as high as 145°C in order to remove water during evacuating. Since solenoid can endure a temperature only up to 48°C, the solenoid valves are set outside the heated box. Three fans (21, 22, 23) are used to cool down the

solenoid, they have one switch (24). So **whenever the heated box is heating, the fans should be switched on!**

The sensors of two MKS BARATRON type 121A absolute pressure transducers are in the heated box linked to the dosing section, one is type 121A01000B, with the range of 1 atm (24); the other is type 121A0001B, with the range of 100 Pa (25). Their working temperature is 0-150°C, their maximum overpressure is 35psia (240kPa). The usage of them will be explained in section 2.2.7.

2.2.4 Temperature control unit

The temperature control unit of this setup includes three heater with controller. The three heaters are the oven in the heated box (28), the heating tape (29) wrapping the gas line between the heated box and the calorimeter, and the oven in the auxiliary thermostat of the calorimeter (30). Each of them is controlled by an EUROTHERM 2416 programmable temperature and process controller (31, 32 and 33).

When the power of a controller is switched on, it runs a self-test sequence for about three seconds and then shows the measured temperature in the upper readout and the setpoint in the lower readout of the display. On this display the setpoint can be adjusted by pressing up and down arrow buttons. Two seconds after releasing either button, the display blinks to show that the controller has accepted the new value.

During measurement of heats of adsorption, the setpoints of all the three controller are always set to 40°C. During evacuation after the measuring cell is connected, the setpoints of them are set to 145°C to evacuate the water inside the system. It should be noticed that, **the setpoint of the controller for the heating tape (32) cannot be set to 145°C directly**, otherwise the temperature increasing rate is so fast that it can raise up to a much higher degree before equilibrium. So just adjust the setpoint 10°C above the measured temperature, when the measured temperature reaches the setpoint, adjust the setpoint 10°C higher again. Observe the blink of the display; when the setpoint reaches 100°C, it can only be set to 5°C higher in one step, and this value should be decreased to 2°C then 1°C before the setpoint is near 145°C.

The temperature control unit should work with the temperature control function of the microcalorimeter. During measurement of heats of adsorption, the working temperature of the

microcalorimeter should be set to 30°C. During evacuation after the measuring cell is connected, the working temperature of the microcalorimeter should be set to 145°C. The temperature control function of the microcalorimeter will be explained in section 3.1.3.

2.2.5 Measuring cell

The measuring cell is made up of stainless steel tubes. It has a sample cell (36), a reference cell (37) and a T-piece. The connection between either cell and the T-piece is a CF flange. The sample cell has a linear feedthrough (35) to crush the sample glass capsule. (Fig 2.13) The connection between the measuring cell and the gas line from the dosing section is a CF flange (34).

The measuring cell is inserted into the microcalorimeter to have a measurement of heats of adsorption. It can be plugged out to input new sample for a new measurement. When input new sample, always open the lower flange of the sample cell in order to avoid that sample particle might go into the reference cell.

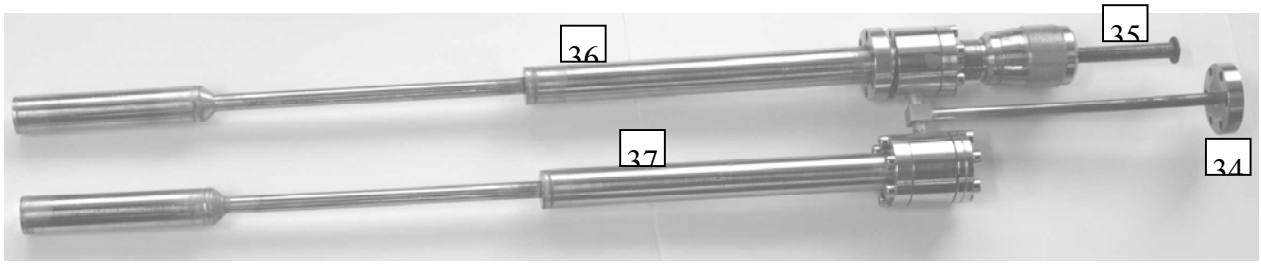

Fig. 2.13 Measuring cell

2.2.6 Microcalorimeter

The kernel of this setup is a SETARAM Tian-Calvet C80 II microcalorimeter. It has an auxiliary thermostat (38), a calorimetric chamber (39) , a CS 32 controller (40), and a power module (41).

The auxiliary thermostat can help the whole measuring cell to have similar temperature. In this setup, the auxiliary thermostat temperature is adjusted 10°C above the temperature of the calorimetric block, so during a measurement of heats of adsorption, the temperature inside the calorimetric block is 30°C while the temperature of the auxiliary thermostat is 40°C.

The CS 32 controller is mainly made up of a CPU card, a keyboard and various acquisition and amplification cards. It controls the power module (40), the oven and the fan of the calorimeter. It receives the electronic signal from the calorimeter, transformed it to the computer "Calvet" (51).

The calorimetric chamber is mounted on a linear adjust device (42), which can be raised up and lowered down, so as to allow the calorimeter to be fixed and the measuring sample to pass through.

See the SETARAM C80II User Manual to know the installation of the calorimeter.

2.2.7 Pressure measurement and control units

1. Pressure measurement unit

The function of pressure measurement units is to measure the pressure in the dosing section. If the calorimeter valve (19) is open, then pressure in the measuring cell is measured because it equals to that in the dosing section. The pressure measurement unit includes an MKS BARATRON absolute pressure transducer with a range of 1 atm (including 25 and 43), an MKS BARATRON absolute pressure transducer with a range of 100 Pa (including 26 and 44) and an MKS PR4000 digital power supply and readout (45); through a voltmeter (46) the pressure data can be input to a computer (49) . Each of the pressure transducer has a sensor (24 and 25). Each sensor is connected

to a signal conditioner: the sensor of 121A01000B should be connected to the signal conditioner 121A01000B (43), and the sensor of 121A00001B should be connected to the signal conditioner 121A00001B (44). The two signal conditioners are then connected to an MKS PR4000 digital power supply and readout (45). The outlet of PR4000 is connected to a voltmeter (46), and then to a computer (49), which is named "Quincy" in the local area network.

It should be noted that the computer receives only one series of signals from PR4000 (through the voltmeter). The tuner of the voltmeter should point to DC 20V. If the pressure data of the 1 atm pressure transducer are needed to input to the computer, then the pin labeled "1S" (with red wire from PR4000) should be inserted to the V/Ω jack and the pin labeled "1GND" (with green wire from PR4000) should be inserted to the ground jack (⏚).If pressure data of the 100Pa pressure transducer are needed to input to the computer, then the pin labeled "2S" (with green wire from PR4000) should be inserted to the V/Ω jack and the pin labeled "2GND" (with yellow wire from PR4000) should be inserted to the ground jack.

During the measurement of heats of adsorption, the pressure data of the 100Pa pressure transducer are needed to input to the computer during experiment.

Normally the PR4000 displays the pressure value measured by both the two pressure transducers, the upper readout is from the 1 atm pressure transducer and the lower one from the 100Pa pressure transducer. The upper readout is in the unit of kPa and the lower one in Pa. If the pressure exceeds 110kPa, both the readouts is "OVERFLOW". If the pressure exceeds 110Pa, only the lower one displays "OVERFLOW". The maximum pressure for both the transducers is 35psia (240kPa), the pressure inside the dosing section cannot exceed that.

The digitals can occasionally shift away from zero when it is indeed vacuum in the dosing section, then the PR4000 need to be rezero by this way:

1) Press the "ENTER" key in the PR4000 front panel several times until it displays the following:

```
AZ1 VLV1 · R1
AZ2 VLV2 · R2
```

2) Press the right arrow key in the PR4000 front panel so that the a cursor will occur under the “AZ1” in the upper display, or press the left arrow key until the cursor occurs under the “AZ1” in the upper display.
3) Press “ENTER” key, then the corresponding digital will be rezeroed.
4) Press “ESC” key in the PR4000 front panel, then it will display the pressure again.

The pressure data input to the computer “Quincy” can be both displayed and logged by programs. The operation will be explained in section 3.2.

2. Pressure control unit

The pressure control unit includes the three pneumatic valves explained in section 2.2.3 (18, 19 and 20), a valve controller (47) and its power adaptor (48), the computer “Quincy” (49) and a power-failure protector (50). Through a program designed in this laboratory (based on NATIONAL INSTRUMENTS LabVIEW), the computer can give signals to the valve controller to open, close or pulse of the three pneumatic valves. These valves can also be open or close through the switches in the front panel of the controller (47) directly.

The power adaptor (48) and the power-failure protector (50) are designed to protect the turbo pump. That is, when the computer “Quincy” is reset or switched on, it will generate random signals during booting in the parallel port which is linked to the valve controller, and might cause an unexpected open of the turbo pump valve (18) and damage the turbo pump if the pressure inside the dosing section is not lower enough; if the gas supply valve (20) is open, it will get even worse. With the power-failure protector (50), the computer cannot restart automatically after a power failure (it can only be switched on again after pressing the green button on the protector). If the computer needs to be switched on, **the power adaptor (48) should be always switched off until the LabVIEW programs in the computer have finished starting!**

3 Operation

3.1 Using the SETSOFT 2000 program

3.1.1 Run SETSOFT 2000

The installation and basic operation of this software is explained in the User's Manual of SETSOFT 2000, here only the operation for the experiment will be showed.

The SETSOFT 2000 program is installed in the computer "Calvet". It is the controlling program for the microcalorimeter. Run it from the Microsoft Windows NT interface by click Start Programme | SETSOFT2000 | Setsoft2000. Then a popup window will occur as Fig 3.1, login by selecting a user's name and typing the correct password. Then click "OK", after one or two minutes of initialization, the program interface will appear.

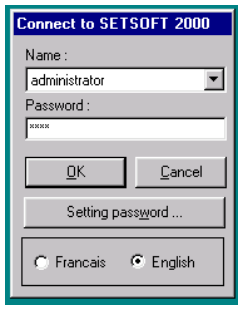

Fig 3.1 Popup window for SETSOFT registration

Whenever the mouse cursor moves near the left edge of an active window of SETSOFT 2000, a toolbar with five buttons will appear (Fig 3.2). The two modules expressed by the upper two buttons (Acquisition and Data processing) are needed for the operation during measurement. These modules can interchange from each to another at any time by clicking a button in the toolbar.

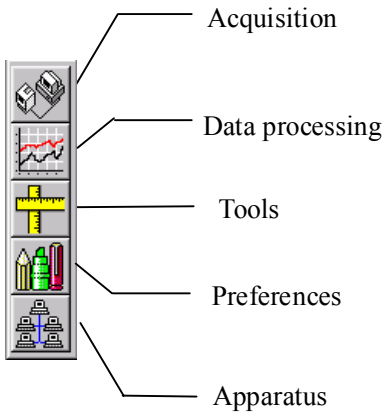

Fig 3.2 Toolbar of SETSOFT 2000

3.1.2 Start collection

Data collection is the function that the SETSOFT 2000 collect the data from calorimeter (through the CS32 controller). To start collection, click the "Acquisition" button of the toolbar, then click the "New Collection" menu item in the "Collection" menu. A pop-up window will appear (Fig 3.3). Select "C80 II" in the "SETARAM apparatus", then press "OK" to confirm. The interface as Fig. 3.4 will appear after a certain time for the computer to execute.

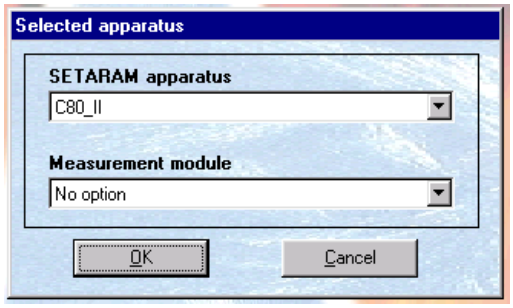

Fig 3.3 Popup window for selecting apparatus

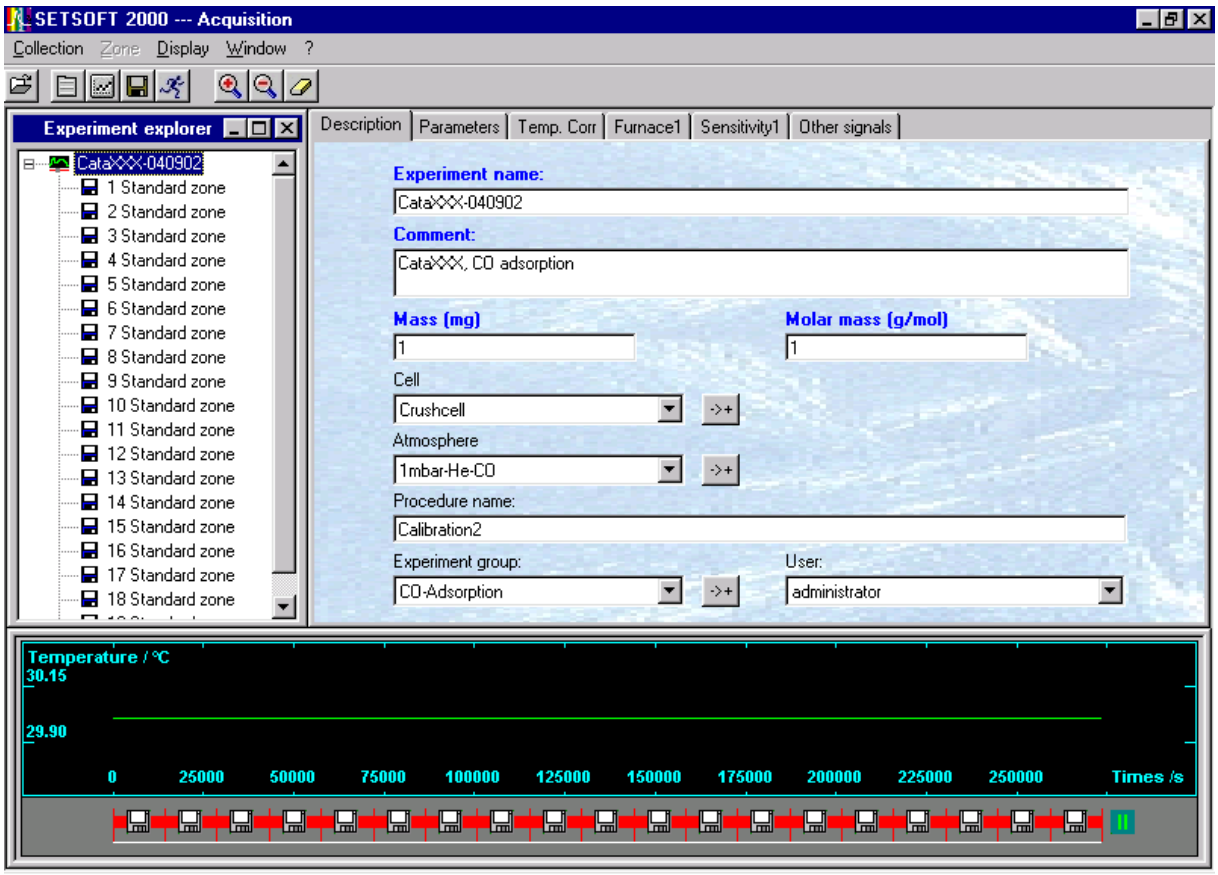

Fig 3.4 An example of the interface to set experiment explorer

In the interface shown in Fig 3.4, the different parameters can be input in the right area. Most important is the name of experiment, it acts also as the file name. Other items will give remarks of an experiment, but they will not affect the experiment result.

In the left area (Experiment explorer area) shown in Fig 3.4, the numbers and features of record zones can be modified, which describes the collection procedure. SETSOFT 2000 program logs the experiment result in data zones, the zones follow one another with time going on. In this setup, each zone for heat flow data collection is generally set as 4 hours long. So for example, if we have 15 zones, SETSOFT 2000 can collect heatflow data for 15 zone x 4 hr/zone = 60 hours.

Each zone can include a series of sequences. There are two type of sequences according to the programmed temperature change: the isotherm one, without temperature change; and the ramp one, with temperature change. The feature to describe a sequences includes its time length, temperature profile type, fan condition and initial temperature. For a ramp sequence, the final temperature should also be defined. Click a zone in the experiment explorers area shown in Fig 3.4 to define a zone, an interface as Fig. 3.5 will appear.

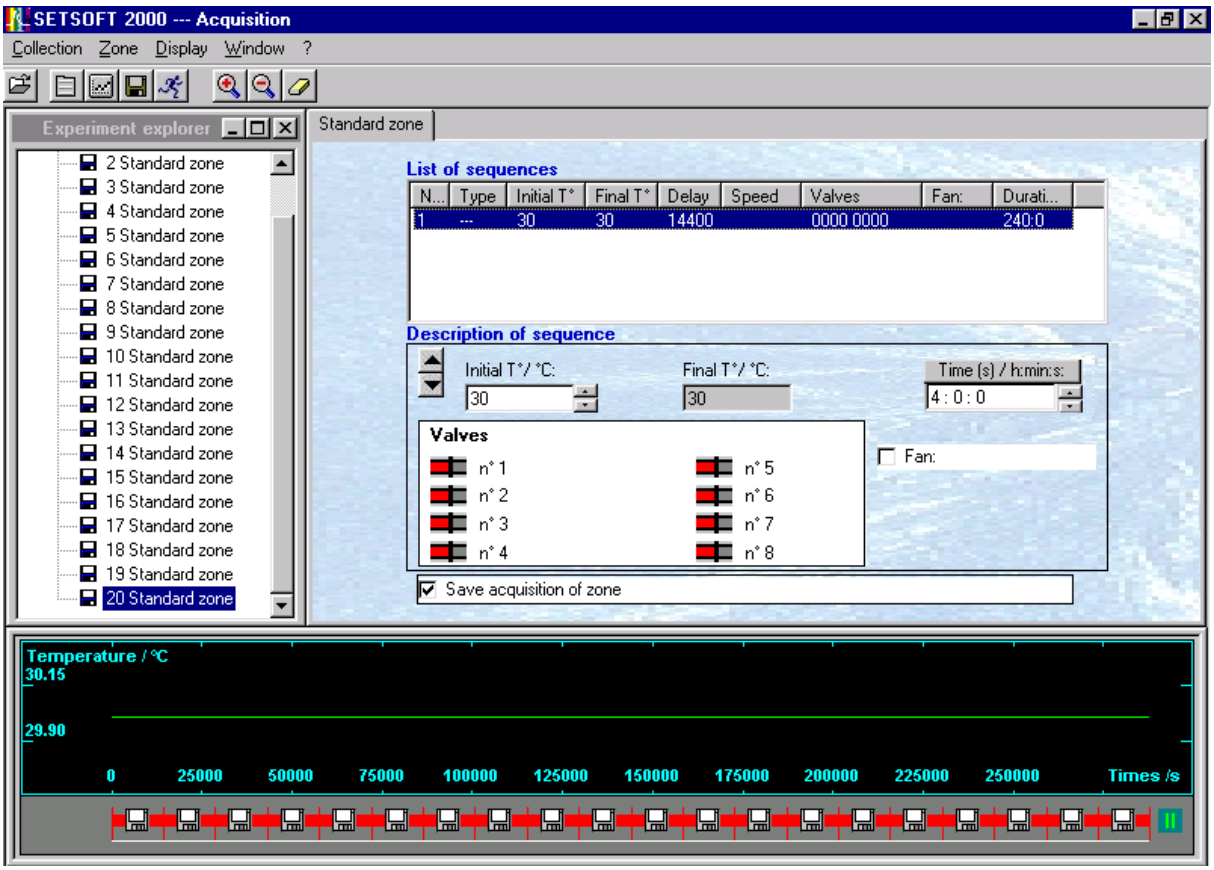

Fig 3.5 An example showing how to define a data zone

For data collection in this setup, there is only one sequence in each zone, its type is isotherm (shown as "---" in the interface). Its initial (and the final) temperature is 30°C. Its length is 4 hours, without fan running. To enter these configuration, just click one zone in the "Experiment explorer" area, then click the sequence in the "List of sequences" area in Fig 3.5.

An important thing is that in such a zone defined above, the data will be collected every 2.9 seconds and there are only 4966 data points in one zone, which is not convenient for data processing. So it is needed to click the "Standard Zone" menu item in the "Zone" menu, to change the "Acquisition period" to 1 in the popup window shown as Fig 3.6, press "OK", then the number of points will change to 14400 automatically.

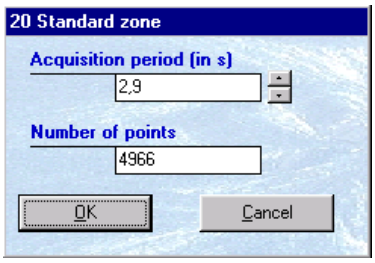

Fig 3.6 Popup window for setting the acquisition period for a data zone

If a new zone is needed, just click the last zone in the “Experiment explorer” area with the right button of mouse, then select “Add zone” | “Standard zone”.

After all the zones are set, select the “Start experiment” menu item in the “Collection” menu, then SETSOFT 2000 begin to collect data. Click the “Real-time drawing” menu item in the “Display” menu, a chart area will appear showing the temperature and heat flow change with time.

Meanwhile, the program can also show other two areas if the corresponding menu items are selected in the “C80” menu, they are “PID” and “Manual programming”. All the areas are shown as Fig 3.7.

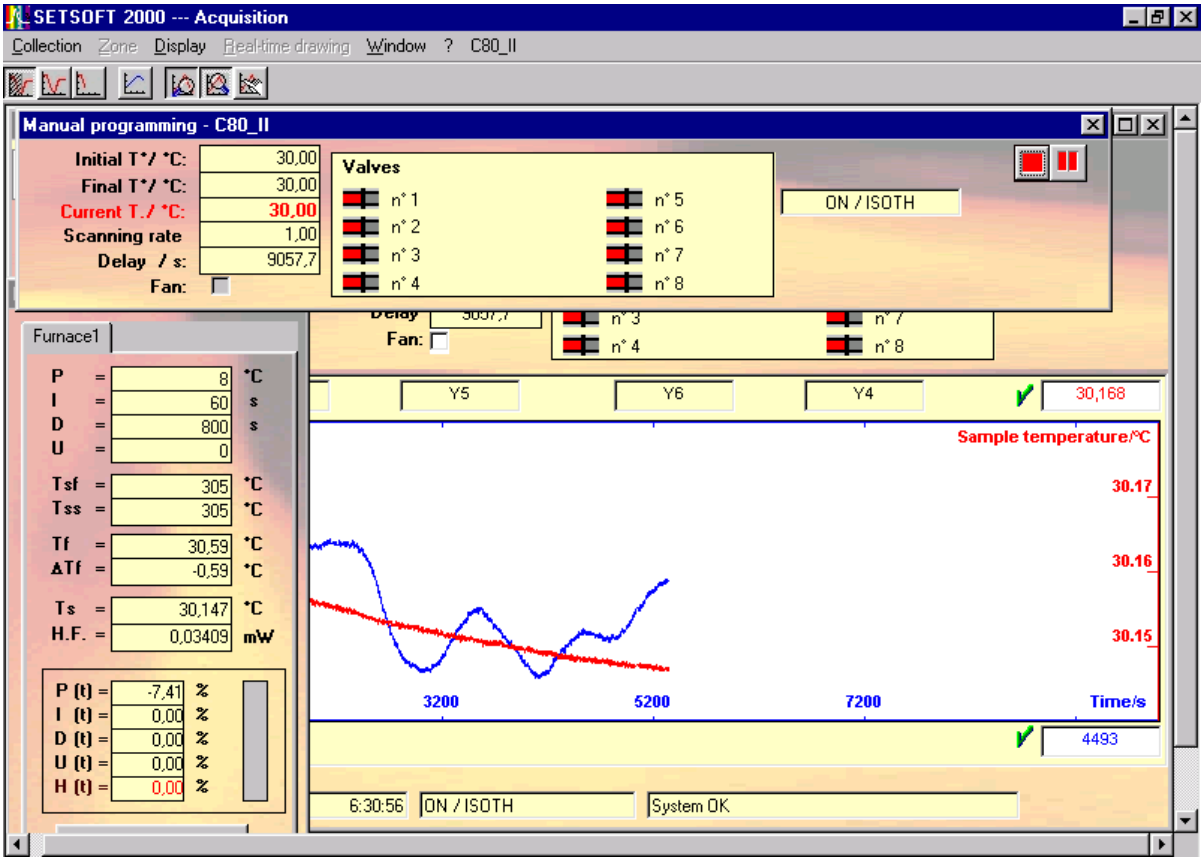

Fig 3.7 Interface with three areas during data collection: chart area, PID area(left), and Manual programming area

The PID area shows the heating actions of the calorimeter. They are Proportional action (P), Integral action (I), Derivative action (D) and Scanning rate (U). The SETARAM company has regulated that P=8, I=60, D=800 and U=0 so as to have good temperature scanning and control. If it is not so, click the “Modify” button in the bottom of the PID area to correct them.

Data collection can be ended by two way: if all zones are finished, the collection will stop automatically; or click the red square button near the right edge of the “Manual programming” area to stop it manually.

It should be noticed that, when a new collection begins, the heat flow and temperature of the calorimeter will change ,which will cost about 1 hour for the calorimeter to get a good baseline.

3.1.3 Direct programming for heating during evacuation

As mentioned in 2.2.4, the temperature of this setup is 145°C during evacuation after it is open to atmosphere. The temperature change of the calorimetric block is programmed by SETSOFT 2000. Select the “New collection” menu item in the “Collection” menu, click the first zone in a new experiment. In the “Standard Zone” area, click a sequence with right button to add new sequence (either “Add isotherm” or “Add ramp”). Add ramp if a temperature increasing or decreasing sequence is needed. Define the initial temperature, final temperature, fan action and delay time of each zone, so a temperature program will be created (Fig 3.8). For an real programming for heating during evacuation, the speed in a temperature-increasing sequence (marked as “/”) can not exceed 2 (°C/min), while the speed in a temperature-decreasing sequence (marked as “\”) can be a random value larger than 1.

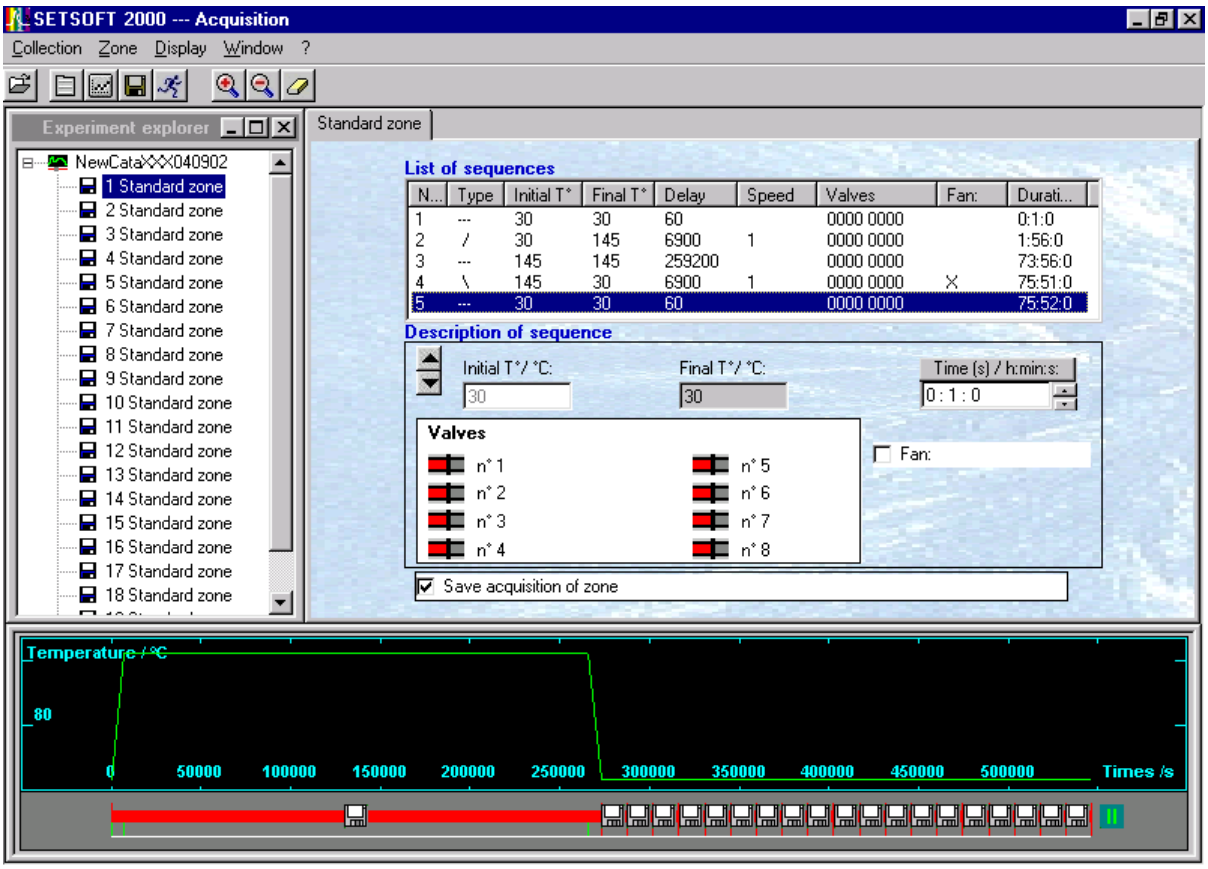

Fig 3.8 Programming temperature for heating during evacuation

It should be noticed that the fan inside the calorimetric block is utilized only in the temperature decreasing sequence. So if such a zone runs, **the fan (blower) switch in the front penal of the calorimeter should be adjusted to "Automatic"**.

3.1.4 Data export

It is convenient to process the data collected by SETSOFT 2000 with MicroCal Origin or Microsoft Excel. So the data need to export.

Click the "Data processing" button in the tool bar (See Fig. 3.2). Then the current collected experiment will appear in the left area of an interface shown in Fig 3.9. Or open an existing experiment by select the "open" menu item in the "Experiment" menu, an opened experiment will also appeared there. Click any a "+" to spread an item. In any spread zone, press the block beside the "HeatFlow", drag it to any of the Y1 –Y6 box, then loose the mouse, a plot showing the heat flow change with time in this zone will appear. Temperature can also be plotted by this way.

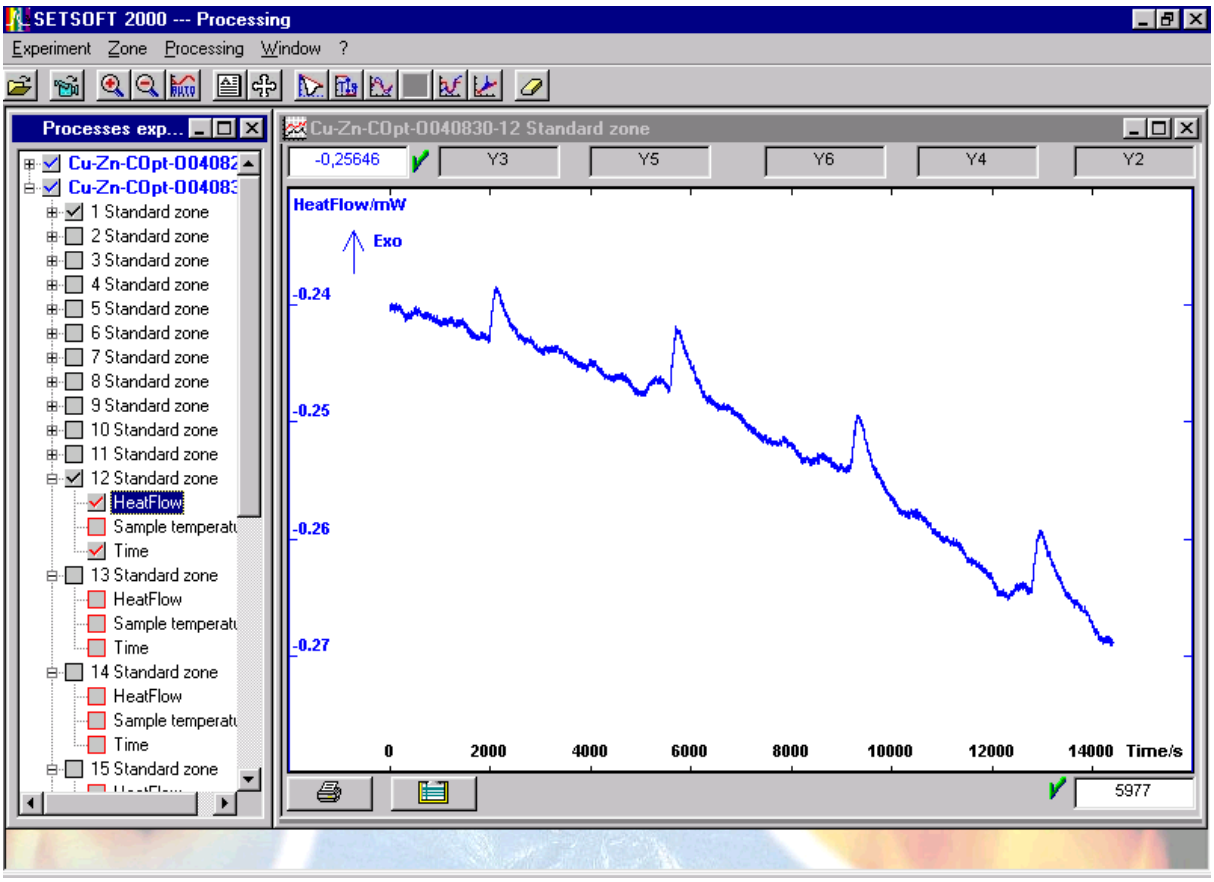

Fig 3.9 Plot the heat flow data of a zone

If a zone is still under experiment, such an operation will bring about an X-axis of only 3 seconds. If such matter happens, just close this zone and open it again after it has finished collection.

After the above plot appeared, the data in the corresponding zone can be exported. Select “Export” menu item in the “Zone” menu, in the popup window define the file name, select the ASCII output type (this determines how the Origin and Excel can open it; it is better to select “ASCII fixed length”), click the “Format” button to define the decimal separator (use “,” for German operating systems); then select “Time” and “HeatFlow” in the Signal(s) selection box in the first popup window, press “OK” to export (Fig 3.10).

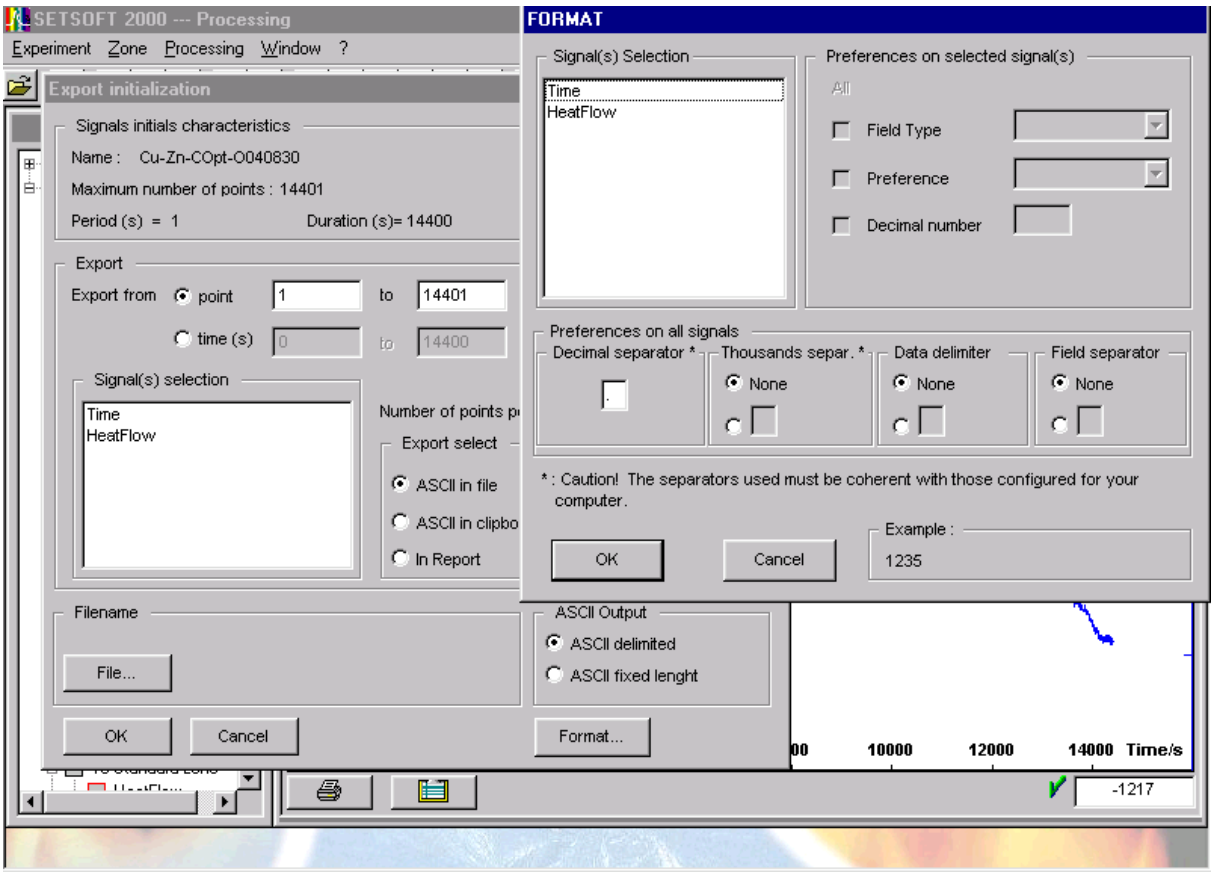

Fig 3.10 Export a data zone to ASCII file

3.2 Operating the pneumatic valves and logging the pressure data

There are three ways to operate the pneumatic valves (18, 19 and 20 in Fig 2.10; all the operation of each pneumatic valve should a solenoid valves, as explained in section 2.2.3):

1. Open or close directly by turn the switches in the valve controller (47 in Fig 2.10);

2. Click the buttons in the controlling program in computer “Quincy”

The interface of the controlling program “VENT-PULS” is shown as Fig 3.11. Click an ON/OFF button to change the status of a valve; or click a PULS button to make the valve open for a short pulse. The minimum pulse time is 0.05 second (but a pulse time shorter than 0.20 second will not open the pneumatic valve in fact), it can be increased with a step of 0.05 second by clicking the arrow button or keying in the text box. When the pressure change shown in PR4000 is not ideal (e. g. it increases too slow after a gas incoming pulse of V3), the pulse time should be adjusted.

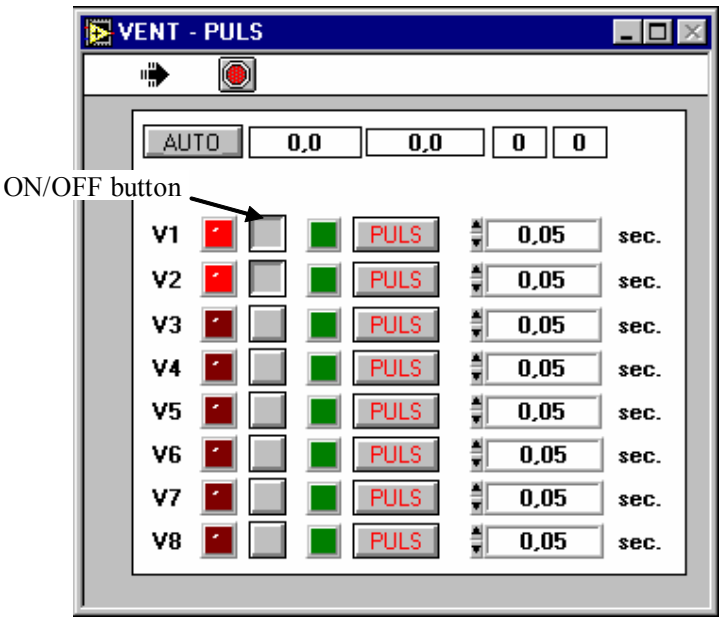

Fig 3.11 Interface of the valve control program "VENT-PULS"

To protect the turbo pump, do not open the turbo pump valve (here the V1) directly when the pressure inside the dosing section (displayed in PR4000) is higher than 100Pa. Besides, if this pressure is between 1kPa-10kPa, just pulse it with a gradually increasing pulsing delay in this manual method. Do not pulse the turbo pump valve (V1) when the dosing section pressure is over 10kPa; use the rough vacuum pump to lower down the pressure.

3. Programmed operation

The above mentioned program "VENT-PULS" can also run a series operation on the valves automatically. Before that, a file should be prepared to define the operation for VENT-PULS. This file can be created with the help of the program "VENT-PULS-EDIT" in computer "Quincy", whose interface is shown as Fig 3.12.

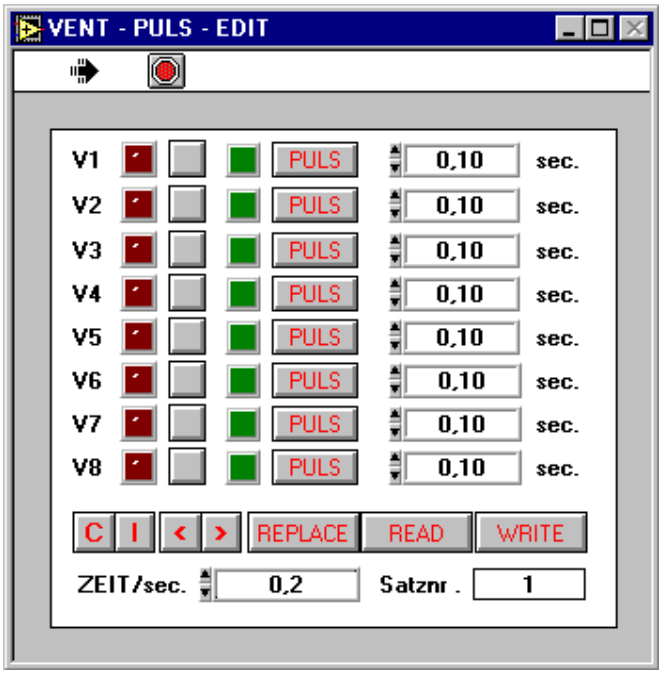

Fig 3.12 Interface of program "VENT-PULS-EDIT"

To create such a file, for each step, press the corresponding key in the interface of VENT-PULS-EDIT (for a pulse, the pulse time should also be defined), then click the "REPLACE" key. Click the ">" button for next step. Click "WRITE" and give a file name to save it.

In this file, the action of the valves are recorded as valve operation with varies time delay. Each operation occupies one line, in 10 columns. The definition is:

0.000	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	10.000
Operation code	Pulse time for the corresponding valve								Delay time

The operation code has a binary meaning. The lowest 8 bits of the binary form of an operation code represent the status of open or close of some of eight valves: 0 is close, 1 is open. The next 8 bits represents the status of pulse or not of eight valves: 1 is pulse, 0 is not pulse. As a result, the useful code (in decimal) for the operation of this set up is :

0.000	1.000	2.000	3.000	4.000	256.000	512.000	1024.000
All valves closed	Open valve 1	Open valve 2	Open both valve 1 and 2	Open valve 3	Pulse valve 1	Pulse valve 2	Pulse valve 3

Here valve 1 refers to the turbo pump valve, valve 2 refers to the calorimeter valve, valve 3 refers to the gas-supply valve.

After the programmed file is ready, press the “AUTO” button in the “VENT-PULS” program, select the file in the dialog box, then the “VENT-PULS” will run the programmed file immediately.

Since a fault operation of valves may damage the turbo pump or evacuate the sample vessel unsuitably, so one should be always cautious when programming the valve actions.

The dosing section pressure data, measured by two Baratron sensors (25 and 26), can be logged by the computer “Quincy” with the program “M4660A-mV-C3” (Fig 3.13). Click the “NEW FILE” button to create a new file in the dialog box, then click “STORE” to begin logging. Noting that only data from one of the two Baratron sensors can be logged (See section 2.2.7). The data are saved as text files.

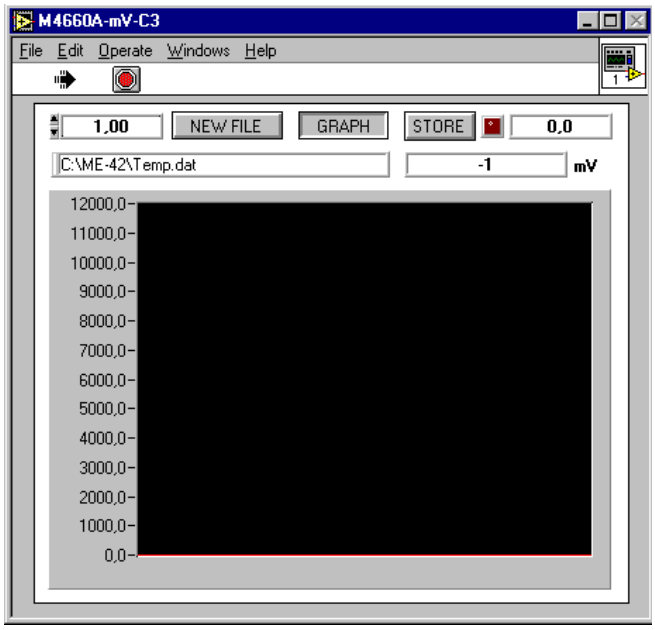

Fig 3.13 Interface of program “M4660A-mV-C3”

3.3 Microcalorimeter calibration

Before the first measurement of heats of adsorption with the microcalorimeter, it should be calibrated.

The mechanism of microcalorimeter calibration is based on Joule’s effect: using a small resistance (about 22 kΩ), give different voltage, measure the current, then compare the electric power with the heat flow of the calorimeter, to get the calibration coefficient (Fig. 3.14).

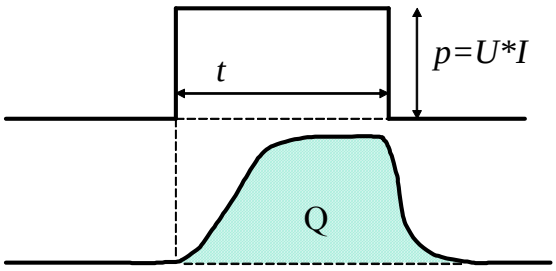

Fig 3.14 Determination of the calibration coefficient by integration

The procedure is (all the number referred the number in Fig. 2.10):

1. Disconnect the measuring cell from the calorimeter, set the resistance with wire into the measuring cell, put the measuring cell in to the calorimetric block, tight the connection (34), combine the two leads of the resistance with a power adapter and an amperemeter. Wrap the heating tape (29) and the isolating materials.

   Be sure to close the turbo pump valve (18) and the calorimeter valve (19), switch off all the three temperature controllers (31, 32 and 33) before disconnect the measuring cell.

2. Close the two shut-off valves for CO and helium (7 and 8), open the shut-off valve for the rough vacuum pump (12), then open the gas-supply valve (20) and the calorimeter valve (19) to evacuate the system with the rough vacuum pump (be sure this pump is switched on).

   When the pressure displayed in PR 4000 (45) is lower than 110Pa, close the gas-supply valve, open the turbo pump valve, so as to get a UHV with turbo pump.

3. Check the calorimeter status, be sure that the fan switch is adjusted to “Automatic”. Switch on the three temperature controllers (31, 32 and 33), set their setpoint to 145°C (the setpoint of the heating tape should increase gradually, see section 2.2.4).

4. Start SETSOFT 2000, prepare enough zones, program a zone for evacuating at 145°C (See section 3.1.3).

5. When the temperature has lowed down to 30°C and the heat flux baseline in SETSOFT 2000 is stable, give the resistance a voltage of 5V for 20min, record the current value, waiting for the baseline to be stable again (for about 30-60min from experience).

6. Such a measurement can be repeated in different pressure of helium: close the turbo pump valve, close the shut-off valve for the rough vacuum pump, open the shut-off valve for helium, pulse the gas-supply valve (the calorimeter valve should be open); observe the pressure value of PR 4000, if the pressure is to high (e. g. over 10kPa), close the shut-off valve for helium, open the shut-off valve for the rough vacuum pump, pulse the gas-supply valve until the pressure in shown in PR4000 is down to nearly 100kPa. Pulse the turbo pump valve to get suitable helium pressure (i. e. 25Pa, 50Pa, 75Pa and 100Pa), measure the Joule effect.

7. The measurement can also be repeated under different voltage (i. e. 2.5V, 10V, 20V and 30V).

3.4 Dosing section volume calibration

The value of dosing section volume is one of the basic parameters to calculate the sample cell volume in each experiment. If any changes happens that might affect the volume of dosing section, then it needs be calibrated. It is obtained on the relationship of the pressures and the volumes of two sections in the gas line; the two sections are the dosing section and the section between gas-supply valve (20) and the shut-off valves (7, 8 and 12). The latter can be connected to a chamber, where a cylindrical metal block with known volume can be put in, to change the volume of this section (Fig 3.15).

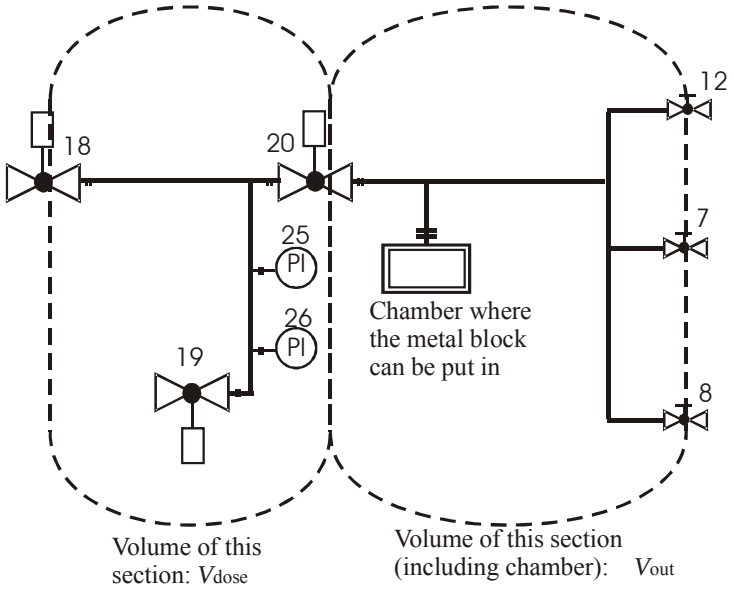

Fig 3.15 The sections for dosing-vessel volume calibration

Labels for the valves and pressure gauges are the same as in Fig. 2.10

There are two ways to measure the dosing section volume:

1. Evacuating the outer part, with a pressure of over 1kPa in the dosing section

Supposing the dosing section volume is V_{dose}, the volume between gas-supply valve (20) and the shut-off valves (7, 8 and 12) is V_{out} (including the chamber). First, a certain amount of gas (using helium here) is filled in V_{dose}, while V_{out} is vacuum. Then open the valve between them (the gas-supply valve), the pressure measured by the Baratron sensors in the dosing section (25 and 26) will drop, assuming from p_{0a} to p_{1a} shown in PR4000. From state equation of ideal gas, we have

$$p_{0a} V_{dose} = p_{1a} (V_{dose} + V_{out}) \tag{3.1}$$

so

$$V_{out}/V_{dose} = p_{0a}/p_{1a} - 1 \tag{3.2}$$

If we fill the chamber in V_{out} with a metal block, the volume of which is known as V_B, then we will have the following relationship repeating the above operation:

$$p_{0a}' V_{dose} = p_{1a}' (V_{dose} + V_{out} - V_B) \tag{3.3}$$

then

$$(V_{out} - V_B)/V_{dose} = p_{0a}' / p_{1a}' - 1 \tag{3.4}$$

From equation (3.2) and (3.4), we have

$$V_{dose} = V_B / (p_{0a}/p_{1a} - p_{0a}'/ p_{1a}') \tag{3.5}$$

That means, with the known value of V_B, by measuring p_{0a} , p_{1a}, p_{0a}' and p_{1a}', we can know the volume of dosing section. So the procedure is:

1) Close the turbo pump valve and the calorimeter valve(they should be always closed in this way), open the valve neighbored to the chamber in the heated box. Connect the voltmeter (46) with the 1GND and 1S pins from PR4000, because this time the pressure inside the dosing section is in rough vacuum (See section 2.2.7).

2) Be sure the shut-off valve for helium and CO is close, open the gas-supply valve (20), open the shut-off valve for the rough vacuum pump (evacuate V_{dose} and V_{out}).

3) Close the shut-off valve for the rough vacuum pump, give a very short open of the shut-off valve for helium then close it; close the gas supply valve (20), record the PR1 outread in the PR4000 (for Baratron-1 atm), this is a p_{0a}.

4) Opening the shut-off valve for the rough vacuum pump for a while so that the pressure V_{out} is about 0.01 mbar, close the shut-off valve for the rough vacuum pump, open the gas supply valve, record the PR1 outread in the PR4000, this is a p_{1a}.

5) If the pressure measured in step 4 is still higher than 5kPa, close the gas supply valve (20), record the PR1 outread in the PR4000 as a new p_{0a}, then repeat (4) to get a new p_{1a}.

6) When the pressure measured in step 4 is lower than 5kPa, repeat from (2) to (5) for several times.

Then open the heated box, close the valve between the camber and the other part of V_{out}, disconnect the camber at the VCR position, take it out from the heated box. Open its mouth (a CF flange), set the metal block inside and close it, connect it again with the other part of V_{out}, open its neighboring valve, repeat the above procedure to get a group of p_{0a}' and p_{1a}'(Fig 3. 15).

2. Evacuating the dosing section, and filling it with a pressure of lower than 100 Pa

In this way, helium in the V_{dose} and V_{out} are in lower pressure initially (p_{0b}), then close the gas supply valve (20), open the turbo pump valve (18) to evacuate the dosing section, then close the turbo pump valve, open the gas supply valve to get a pressure p_{1b}.

In this time,

$$p_{0b}\, V_{out} = p_{1b}\, (V_{dose} + V_{out}) \tag{3.6}$$

so

$$V_{out}/V_{dose} = p_{1b}/(p_{0b} - p_{1b}) \tag{3.7}$$

If V_{out} is filled with the metal block with volume V_B,

$$p_{0b}'\, (V_{out} - V_B) = p_{1b}'\, (V_{dose} + V_{out} - V_B) \tag{3.8}$$

then

$$(V_{out} - V_B)/V_{dose} = p_{1b}'/(p_{0b}' - p_{1b}') \tag{3.9}$$

From equation (3.7) and (3.9),

$$V_{dose} = V_B / [p_{1b}/(p_{0b} - p_{1b}) - p_{1b}'/(p_{0b}' - p_{1b}')] \quad (3.10)$$

So with the known value of V_B, by measuring p_{0b} , p_{1b}, p_{0b}' and p_{1b}', the volume of dosing section can also be known. The procedure is:

1) Close the turbo pump valve and the calorimeter valve, open the neighboring valve of the chamber, connect the voltmeter (46) with the 2GND and 2S pins from PR4000. (See section 2.2.7)

2) Be sure the shut-off valve for helium and CO is close, open the shut-off valve for the rough vacuum pump and the gas-supply valve (evacuate V_{dose} and V_{out}), then close the gas- supply valve, open the turbo pump valve to go on evacuating.

3) Close turbo pump valve, give a very short open of the shut-off valve for helium then close it; close the gas supply valve (20), open the shut-off valve for the rough vacuum pump, by pulsing the gas supply valve, lower down the PR1 outread in the PR4000 to about 1kPa, then close the shut-off valve for the rough vacuum pump, open the gas supply valve, by pulsing the turbo pump valve to make the PR2 outread in the PR4000 lower than 100Pa and record it, this is a p_{0b}.

4) Close the gas supply valve, open the turbo pump valve to evacuate the dosing section, then close the turbo pump valve and open the gas supply valve, the gas will come from V_{out} to V_{dose}; record the PR1 outread in the PR4000 at ecquilibrium, this is a p_{1b}.

5) If the pressure measured in step 4 is still higher than 5Pa, record it as a new p_{0b}, then repeat (4) to get a new p_{1a}.

6) When the pressure measured in step 4 is lower than 5Pa, repeat from (2) to (5) for several times.

After setting the metal block inside the V_{out}, repeat the above procedure to get a group of $p_{0b}'$and p_{1b}'. Of course these two way can be done with filling of the metal block only once.

The volume of the dosing section is calculated to be 39.38cm^3 in this setup.

After calibration, close the valve between the chamber and other parts of the setup.

3.5 Measuring cell volume calibration

Since the volume of the dosing section (V_{dose}) are known, it is easier to measure the volume of the measuring cell volume. The principle is, evacuate both of the dosing section and the measuring cell, then close the valve between them (i.e. the calorimeter valve 19), fill the dosing section with an certain pressure of helium (p_{dose}), then connect these two parts to get a new pressure (p_{eq}). From state equation of ideal gas

$$p_{dose}\, V_{dose} = p_{eq}(V_{dose}+V_{cell}) \tag{3.11}$$

then

$$V_{cell} = V_{dose}\,(p_{dose} - p_{eq})/\, p_{eq} \tag{3.12}$$

The measuring procedure is:

1. The gas supply valve (20) and the shut-off valve for CO should be always closed; open the shutoff valve for the rough vacuum pump.

2. At lower pressure (<100Pa) in the dosing section and the measuring cell, open both of the turbo pump valve and the calorimeter valve to evacuate the dosing section and the measuring cell.

3. Close the calorimeter valve (keep the cell in vacuum), close the turbo pump valve, close the shutoff valve of the rough vacuum pump, then open the shutoff valve for helium, pulse the gas supply valve.

4. If the pressure shown in PR 4000 is higher than 100Pa, pulse the turbo pump several times until the pressure is between 85-100Pa; record the pressure, this is p_{dose}.

5. Open the calorimetric valve (19), the pressure will drop. Record the equilibrium pressure, this is p_{eq}. With these two pressure values, V_{cell} can be calculated out.

6. Repeat (2)-(5) for 10 to 25 times, in order to get a statistic result of V_{cell}.

The pressure data are generally recorded by keying in a Microsoft Excel file for data processing (See section 4.1.2). The measuring cell is about 85cm^3, varying due to the difference of the position of the screw (35) and the volume of the glass capsule.

3.6 Preparing samples for measurement

The main type of sample measured with this setup is the catalyst for methanol synthesis, including ZnO-alumina, Cu-ZnO-alumina, Cu-ZnO samples etc. The suitable size of sample for the measurement is 250-355μm. Some samples need reduction and/or other pretreatment.

3.6.1 Sample particle resizing

If the size of sample is not suitable, it need to be resized. The procedure is:

1. If the original size is smaller than suitable size, make the sample powder as tablets with a press (Fig. 3.16).

2. Grind the tablets (or the powder, if its the original size is large than suitable size) with an agate mortar .

3. Collect the ground powder to a series of screen (a 355μm screen, a 250μm screen and a container) in the order of coarser to finer from upper to lower, sift it, collect the powder with suitable size.

4. Make the powder inside the finer screen to tablets, grind it with the powder inside the coarser screen and repeat the above steps, until enough sample is obtained.

All the tools mentioned above, including the tools for the press, the mortar with the pestle, the screens and the brush to clean them are special in the lab for the methanol synthesis catalysts.

Fig. 3.16 A Perkin-Elmer hydraulic hand press

3.6.2 Operation before and after pretreatment

Fig 3.17 shows the reactor for sample pretreatment. It includes a steel U-shaped tube as a reactor and a Pyrex NMR tube for sample sealing. The complete cell consists of UHV components. Before pretreatment, the reactor should be prepared in the following procedure:

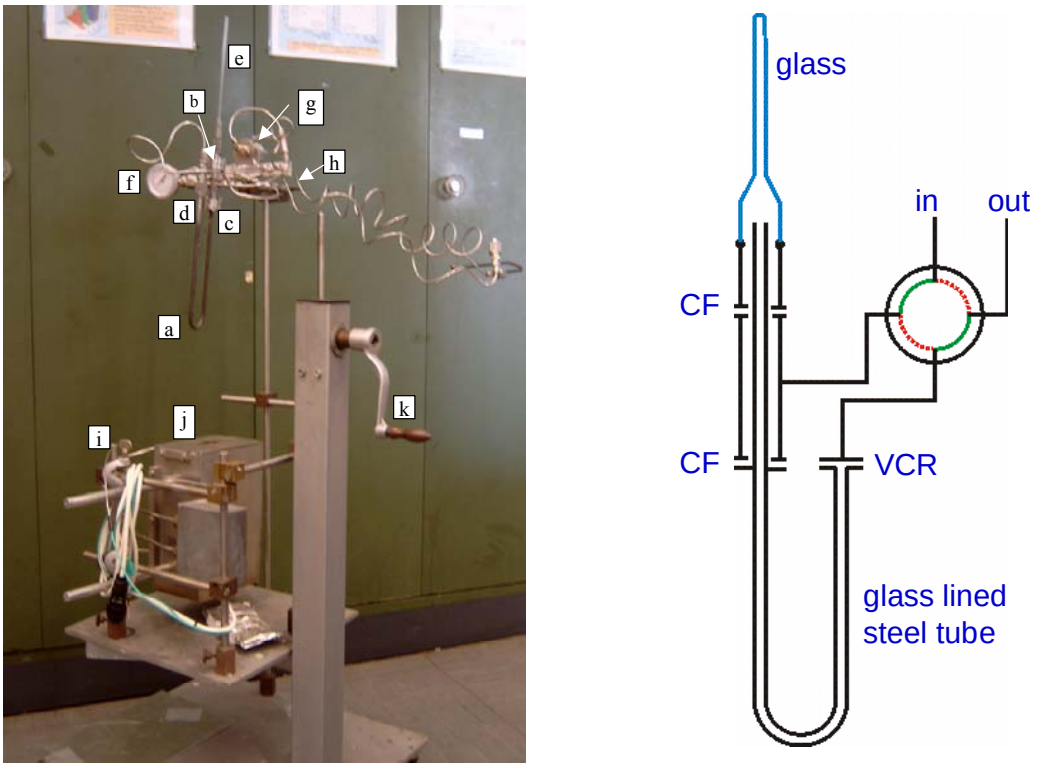

Fig 3.17 Device for pretreatment of catalysts

(a) U-tube; (b) Upper CF flange; (c) Lower CF flange; (d) VCR fitting; (e) Pyrex NMR tube; (f) pressure gauge; (g) 4-way valve; (h)clamp; (i) thermocouple; (j) oven; (k) linear adjust device

1. weigh the sample with suitable particle size for 0.1000-0.1100 g in a special glass boat (Fig 3.18).

2. Disconnect the U-shaped tube at the lower CF flange (c) and the VCR (d) (if the Pyrex NMR tube is still connected to the reactor, disconnect it at the upper CF flange b), use compressed air in the laboratory to blow the small quartz-wool bar out (if there is); use distilled water wash the U-tube three time, then wash it acetone.

3. Connect the CF flange (c) and the VCR fitting (d) of the U-tube to the device, twist a small amount of quartz wool to a 2 cm plug with glove, insert it into the flange branch of the U-tube, use a metal stick in the quartz wool bar side of the U-tube and a soft Teflon stick in the opposite side to adjust the position of the quartz wool bar, (about 1cm above the bottom of the U-tube branch).

This quartz wool bar is applied to prevent the catalyst particle from falling down to the bottom of the U-tube or even blown to the filter between the U-tube and the 4-way valve, so it should be neither too tight nor too loose.

4. Put the sample in the glass boat into the U-tube with a special glass funnel (See Fig 3.18) at the mouth above the upper CF flange.

5. Connect the Pyrex NMR tube (e) to the device at the CF flange (b). Be careful not to damage the Pyrex NMR tube, especially in the wide part near the connection of glass and metal, because it is quite difficult to fabricate such a connection.

6. Connect the inlet and outlet of the device to the corresponding gas line (through 2 VCR connections), set the thermocouple to the right position (the end of the thermocouple should be 1 cm above the bottom of the U-tube), lift the oven up (j) so that the U-tube is in the oven chamber.

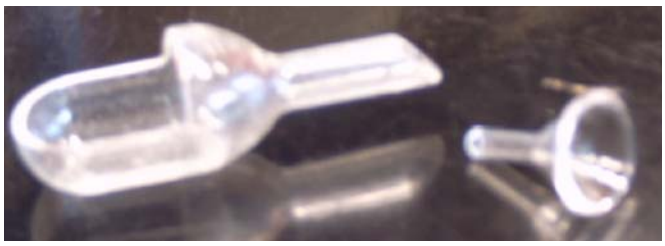

Fig 3.18 The glass boat and funnel to contain and transfer sample

After the pretreatment, do the following steps to get a sample capsule:

1. Switch off the oven, move it down, wait until the U-tube is cooled down;

2. Switch the 4-way valve (g) so that the U-tube is closed. Now the U-tube should be filled with helium, which flows through the reactor in the last step of pretreatment.

3. Disconnect two VCR connections at the inlet and outlet of the reactor, loose the screw of the clamp (h), turn around the U-tube with the Pyrex NMR tube so that the catalyst particle can fall from the U-tube down to the Pyrex NMR tube.

4. Connect the inlet and outlet of the device to the rough vacuum pump (Fig 2.12), turn the switch of the pump to this gas line.

5. Observing the pressure gauge (f) of the device, open the 4-way valve shortly, so that the relative pressure inside the Pyrex NMR tube drop to between negative 0.5-0.8 atm.

6. Use a blowtorch (Fig 3.18) to melt and seal the Pyrex NMR tube to get a capsule, the length of the capsule should be controlled as about 95mm. Place the capsule to a safe place nearby then quench the blowtorch with two hands. **It is impossible to quench the blowtorch with only one hand**!

7. Preserve the capsule; disconnect the rest part of the Pyrex NMR tube and hand it with a glass tube to the glass workshop to have a new Pyrex NMR tube.

Fig 3.19 The blowtorch to seal the capsule

3.7 Operation of dosing cycles

A dosing cycle is to make the adsorbtive pooled in the dosing section to mix with the gas in the measuring cell, so that the partial pressure of adsorbtive will increase in the measuring cell, and the adsorption will go on. Before each mixing, there should be no serious pressure difference between the dosing section and the measuring cell, otherwise a work of gas expansion will bring about an error in the measurement of heat flow. So the preparation of suitable pressure in the dosing section and measuring cell is very important.

In the start of a dosing cycle, the dosing section and the measuring cell are connected and the adsorbtive partial pressure is at equilibrium with the coverage of adsorbate on adsorbent. Then isolate the dosing section and the measuring cell, evacuate the former then fill it with adsorbtive, adjust to a suitable pressure, link the dosing section and the measuring cell again, wait until equilibrium, this is the end of a dosing cycle and the start of the next dosing cycle. A dosing cycle can be fulfilled by the following steps:

1. Make sure that the calorimeter valve is open, the turbo pump valve and the gas supply valve are closed.

2. Be sure the pressure shown in PR 4000 is 80-100Pa. It is very important that before the first cycle, the helium pressure is 85-100Pa in the dosing section and measuring cell (with calorimeter valve being open). The helium comes either from the crushed sample capsule or from the helium supply. If the helium from the capsule is not enough or no helium in the dosing section (e.g, for a non-encapsulated sample, or for a sample under repeating measurement), do the following steps:

    1) Make sure that the calorimeter valve is open, the turbo pump valve, the gas supply valve and the shut-off valve for CO are closed; close the shut-off valve for the rough pump, open the shut-off valve for helium.
    2) Pulse the gas supply valve to have a pressure of over 85Pa shown the PR4000, then close the shut-off valve for helium, open the shut-off valve for the rough pump.
    3) If the pressure displayed in PR4000 exceeds 1kPa, pulse the gas-supply valve to have a pressure in PR4000 between 100Pa and 1kPa.
    4) If the pressure displayed in PR4000 exceeds 100Pa, use the pulse the turbo pump valve to have a value between 85Pa and 100Pa.

3. Create a data file and start to log pressure data (See section 3.2).

4. Wait until the baseline is good (that means, the noise and the baseline shift will be small enough compared with heat flow peaks). For the first dose, pressure change in the setup during this waiting period can be applied to calculate leakage rate.

5. Close the calorimetric valve and open the turbo pump valve so as to evacuate the dosing section for about 1 minutes (the readout of the lower readout of PR4000 should drop to 0).

6. Fill the dosing section with CO by the following step:

    1) Close the turbo pump valve, close the shut-off valve for rough vacuum pump, open the shut-off valve for CO.
    2) Pulse the gas supply valve to have a pressure of over 85Pa shown the PR4000, then close the shut-off valve for CO, open the shut-off valve for the rough pump.
    3) If the pressure displayed in PR4000 exceeds 1kPa, pulse the gas-supply valve to have a pressure in PR4000 between 100Pa and 1kPa.
    4) If the pressure displayed in PR4000 exceeds 100Pa, use the pulse the turbo pump valve to have a value between 85Pa and 100Pa.

7. open the calorimeter valve, CO goes to the measuring cell so the adsorption begins, a heat flow peak happens in the display of SETSOFT 2000. Then repeat from step 4.

The necessary amount of cycles varies with different samples, from <10 cycles to 50 cycles. Samples are often measured twice. After the last dose of the first measurement, open the turbo pump valve to evacuate overnight and then close the turbo pump valve, start from step 1. of this section.

It is convenient to apply the automatic running function of VENT-PULS (see section 3.2), but before that, it is necessary to know the times of pulses of the gas supply valve and the turbo pump valve (and the delay time of each pulse) to get a suitable CO pressure in the dosing section in step (4) of the above. So that should be try it several time (during trying, the calorimeter valve should be always closed!). Then create an automatic running file with the help of VENT-PULS-EDIT (section 3.2).

The following is the content of an automatic running file sample for a dosing cycle:

```
0,000 0,100 0,100 0,100 0,100 0,100 0,100 0,100 0,100 10,000
1,000 0,050 0,050 0,050 0,050 0,050 0,050 0,050 0,050 30,000
0,000 0,050 0,050 0,050 0,050 0,050 0,050 0,050 0,050 30,000
1024,000    0,050 0,050 0,350 0,050 0,050 0,050 0,050 0,050 5,000
256,000     0,250 0,050 0,050 0,050 0,050 0,050 0,050 0,050 5,000
256,000     0,250 0,050 0,050 0,050 0,050 0,050 0,050 0,050 5,000
256,000     0,250 0,050 0,050 0,050 0,050 0,050 0,050 0,050 5,000
256,000     0,250 0,050 0,050 0,050 0,050 0,050 0,050 0,050 5,000
256,000     0,250 0,050 0,050 0,050 0,050 0,050 0,050 0,050 5,000
256,000     0,250 0,050 0,050 0,050 0,050 0,050 0,050 0,050 5,000
```

```
256,000     0,250 0,050 0,050 0,050 0,050 0,050 0,050 0,050 20,000
2,000 0,050 0,050 0,050 0,050 0,050 0,050 0,050 0,050 2700,000
```

The upper operations mean that, the cycle begins with all valve closed for 10 seconds; then open the turbo pump valve, delay 30 seconds (to evacuate the dosing section); close the turbo pump valve, delay 30 seconds; pulse the gas supply valve for 0.35 second, delay 5 seconds; pulse the turbo pump valve seven times, in each time it pulses 0.25 second and delay 5 seconds except that the delay time after the last pulse is 20 seconds; finally open the calorimetric valve (to start adsorption), delay 2700 seconds (45 minutes) so that the baseline can be good.

3.8 Measurement of heats of adsorption

A typical measurement of heats of adsorption, with encapsulated sample, includes the following steps:

1. Installation of the measuring cell with new sample
    1) close the turbo pump valve (18), close the shut-off valves for CO and helium (7 and 8);
    2) close all of the three temperature controller (31, 32 and 33);
    3) unwrap the isolating materials and the heating tape (29) around the upper part of the measuring cell with glove, disconnect the CF flange (34);
    4) lower down the calorimeter through the linear adjust device (42), plug the measuring cell a bit out; if it is two tight, turn the calorimetric block slightly; lean the calorimeter a bit to the left side in order to move out the measuring cell;
    5) open the lower connection of the sample cell (see section 2.2.5), if there samples inside, collect it;
    6) make sure the length of the sealed glass capsule containing sample is 95mm, put the sample glass in carefully with some tools, then close the sample cell;
    7) lean the calorimeter slightly to insert the measuring cell into the calorimeter, lift the calorimeter through the linear adjust device till the distance between the two parts of the flange (34) is about 1-2mm, place the copper gasket, lift the calorimeter through the linear adjust device for the last distance, connect the flange, wrap the isolating materials with gloves (be careful that the different wires should not touch one another).

2. Evacuating with heating
    1) create a new collection in SETSOFT 2000 (see section 3.1.2), program the heating process in the first zone (see section 3.1.3), start acquisition;
    2) switch on the fans for the pneumatic valves (24);

3) open the three temperature controllers (31, 32 and 33), adjust the setpoint of those for the heated box and auxiliary thermostat (31 and 33) as 145°C directly, adjust that for the heating tape gradually to 145°C (see section 2.2.4);
4) make sure the turbo pump valve (16) is closed, open the calorimeter valve (19), be sure the shutoff valve for CO and helium (7 and 8) are closed, open shut off valve for the rough vacuum pump (12), open the gas supply valve (20), use the rough vacuum pump to evacuate the system to a pressure lower than 100Pa;
5) close the gas supply valve (20), open the turbo pump valve (18) to evacuate the system with the turbopump;
6) check the pressure presented by the full range pressure gauge (16), if the readout can not drop down to 10^{-4} mbar in ten minutes, then the system is not leakage tight, it need re-installation. Otherwise evacuate the system for 72 hours.

3. Preparation for measurement
    1) adjust the three temperature controller to 40°C, it will cost a night for the system to cool down;
    2) prepare a new experiment in the SETSOFT 2000 program, make sure that the zone time are enough (see section 3.1);
    3) switch off the fans for the calorimeter one hour before the measurement;
    4) close the valve for turbo pump (18), with the calorimetric valve (19) opening, test the leakage rate of the system for about 10 minutes, a leakage rate lower than 0.003Pa/min is ideal; then open the valve for turbo pump (18).

4. Start measurement
    1) as the temperature is ideal (about 30°C, or 5°C above room temperature, whichever is warmer), close the valve for turbo pump (18) with the calorimetric valve (19) being open, unwrap the isolating materials in the upper part of the measuring cell, turn the linear motion feedthrough(35) to crush the sample capsule, and then turn it back to the uppermost position (be careful the electric currents in the heating tapes);
    2) if there is an overflow, pulse the valve for turbo pump for several times to get a pressure of 80-100Pa in the cell;
    3) create a file for pressure logging, start data logging (see section 3.2 and 3.7; the first part of the pressure data will be used to calculate the leakage of the system);
    4) switch off the fans for the pneumatic valves;
    5) wrap the isolating materials in the upper part of the measuring cell;

6) prepare the file for automatic dosing (see section 3.2 and 3.7);
7) start acquisition of the prepared experiment in SETSOFT 2000 program;
8) close the shutoff valve for the rough vacuum pump (12), open the shutoff valve for CO (7), the absolute pressure should be 1 bar;
9) When the baseline is fine, start the first dosing, either manually or automatically (See section 3.7).

5. After first measurement
   1) after all the doses finishes, stop the pressure data-logging, open both of the turbo pump valve and the calorimeter valve to degas the sample with adsorbates overnight;
   2) close the valve for turbo pump (18), close the shutoff valve for CO, open the shutoff valve for the rough vacuum pump (12), then wash this part several times with helium with the alternative open and close of the two shutoff valves for helium and rough vacuum pump (8 and 12), close the valve for mechanic pump, open that for helium;
   3) calibrate the measuring cell volume with helium (see section 3.5);
   4) at the last step of measuring cell calibration, close the calorimeter valve to preserve helium with a pressure of 85-100Pa in the measuring cell, open the valve for turbo pump evacuate the dosing section alone;
   5) when the baseline is fine, close the helium shutoff open the valve for CO, begin the second automatic adsorption;
   6) after twice measurement, if no further measurements are needed, disconnect the measuring cell, take out the sample, pick up glass chippings and weigh the sample.

4 Data processing

4.1 Getting the adsorption isotherm

4.1.1 Principles

From the steps of a dosing cycle described in section 3.7, a series of pressure change will be logged in the computer "Quincy", plotted as the dashed line in Fig. 4.1.

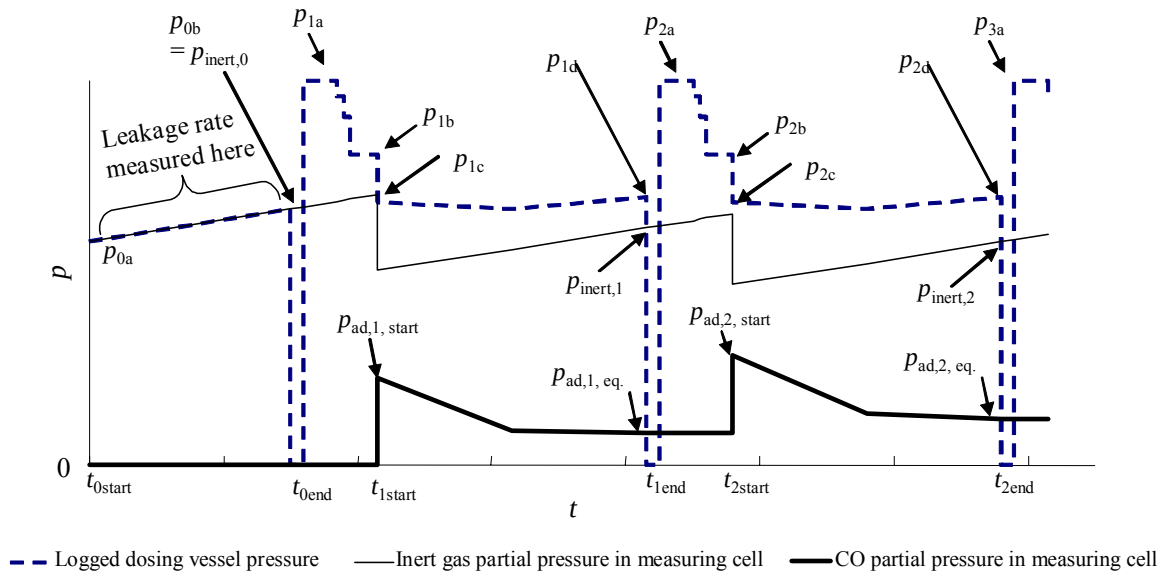

Fig 4.1 Pressure change during dosing cycles

The actions that bring about the change of logged dosing section pressure includes:

p_{0a}- start pressure at t_{0start}, with the calorimeter valve open and the turbo pump valve closed;

p_{0b}- pressure at t_{0end}, increase from p_{0a} due to leakage;

p_{1a}- a overflow pressure (>110Pa) after closing the calorimeter valve, opening the turbo pump valve, and then a pulse of gas supply valve;

p_{1b}- a suitable pressure (85-100Pa) after several pulses of turbo pump valve;

p_{1c}- open the calorimetric valve;

p_{1d}- pressure at t_{1end}, change from t_{1start} due to adsorption and leakage.

Based on the meaning of pressure change in dosing section, the amount of adsorbate can be calculated out in the following way:

1. Calculating the leakage rate of the system

$$Lrate = \text{slope of the pressure change from } t_{0start} \text{ to } t_{0end} \quad (4.1)$$

It can be calculated out with a Microcal Origin 6.0 program.

2. Calculating the inert gas pressure in the measuring cell

The inert gas includes helium and the air leaked from outside. The inert gas partial pressure in the measuring cell at the end of each dosing cycle depends on two parameters: this partial pressure at the end of last dose (e. g. at $t_{1\text{end}}$, $t_{2\text{end}}$, …$t_{n\text{ end}}$ etc.) and leakage amount during this cycle. So it can be expressed as

$$p_{\text{inert, n}} = p_{\text{inert, }n\text{-1}} \times V_{\text{cell}}/(V_{\text{cell}}+V_{\text{dose}})+Lrate \times(t_{n\text{ end}} - t_{n\text{-1 end}}) \quad (4.2)$$

The change of inert gas partial pressure in the measuring cell is shown in Fig 4.1.

3. Calculating the amount of adsorbate

At the end of each dose, when the adsorption is at equilibrium, the partial pressure of the adsorbtive gas is the difference between the total pressure and the inert gas partial pressure:

$$p_{\text{ad, }n\text{, eq.}} = p_{n\text{d}} - p_{\text{inert, }n} \quad (4.3)$$

At the start of each dose, the partial pressure of the adsorptive can be calculated out from the mixing:

$$p_{\text{ad,}n\text{, start}}=(p_{\text{dose,}n} \times V_{\text{dose}}+ p_{\text{ad,eq,}n\text{-1}} \times V_{\text{cell}})/(V_{\text{cell}}+V_{\text{dose}}) \quad (4.4)$$

The increasing amount of adsorbate during a dose can be calculated out from the difference between the start pressure and the end pressure of adsorptive:

$$n_{\text{ad,}n} =(p_{\text{ad,}n\text{, start}} - p_{\text{ad,eq, }n}) \times (V_{\text{cell}}+V_{\text{dose}})/(R_{\text{gas}}\, T)/m_{\text{sample}} \quad (4.5)$$

The isotherm of adsorption can be directly plotted with the equilibrium adsorptive partial pressure and the increasing amount of adsorbate.

4.1.2 Using the Microsoft Excel template file for calculation

All the above calculation will be processed by a Microsoft Excel file, which acts as a template. Key in the parameters and the pressure data needed, all the in-between and final results explained above will be obtained. The needed data include:

1. Key in the leakage rate, sample mass and dosing section volume values in the “RUN CONDITION” area.

RUN CONDITIONS		
Sample mass:	0,107	g
Sample area:	0,0	m^2/g
Dosing Section Temp:	40,0	°C
Ads/Calorimeter Temp:	30,0	°C
Dosing Section Volume:	39,13	cm^3
Cell Section Volume:	84,49	cm^3
Leak Rate:	6,19E-05	Pa / s
Leak Rate:	3,7E-03	Pa/min

2. Key in the data for the measuring cell volume calibration in the “CELL VOLUME CALCULATION” area, in order to get the dosing section volume. These data can be also input in the same time of measuring cell volume calibration.

CELL VOLUME CALCULATION			
Dose #	**Pdose / Pa**	**Peq / Pa**	**Vcell / cm^3**
1	98,30	31,12	84,47
2	92,18	29,17	84,53
3	85,18	26,96	84,50
4	95,82	30,33	84,49
5	87,26	27,61	84,54
6	98,60	31,21	84,49
7	89,86	28,45	84,47
8	91,66	29,02	84,46
9	93,69	29,66	84,48
10	94,84	30,02	84,49
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
		Average:	84,49
		Std Dev:	0,03
			0,03%

3. Open the pressure data file with Microcal Origin program, draw a *p*-*t* plot, collect the p_{nb} and p_{nd} values of each dose, input them in the “CHEMISORPTION ISOTHRM DATA” area. The dosing time can also be calculated out from the *p*-*t* plot.

CHEMISORPTION ISOTHERM DATA			
Dose #	Pdose / Pa	Peq / Pa	Dose Time / min
		88,96	
1	83,82	86,75	112,6
2	86,73	86,45	37,3
3	87,88	86,68	37,1
4	88,67	87,11	37,1
5	89,05	87,54	37,1
6	88,69	87,76	37,1
7	88,22	87,72	37,1
8	88,88	87,95	37,1
9	89,55	88,25	37,1
10	89,90	88,65	37,1
11	89,42	88,71	37,1
12	91,74	89,48	37,1
13	91,60	89,97	37,1
14	91,99	90,43	37,1
15	93,82	91,27	37,1

After that, adjust the data series source and the axis scales in the "ADS ISOTHERM" worksheet of the Excel file, then the adsorption isotherm of a measurement will be obtained.

4.2 Getting the differential heats

The differential heat of each dose (q^{diff}) is the heat generated during this dose divided by the increasing adsorbate amount during this time and by the mass of adsorbents; the heat generated during each dose is the integral of heat flow measured by calorimeter with time:

$$q^{diff}_n = \Delta Q_n / n_{ad,n}/m = \int \phi dt / n_{ad,n}/m \qquad (4.6)$$

The integral of a heat flow peak can be processed with Microcal Origin software:

1. Run Origin program, import a zone file (a zone file is exported by Setsoft 2000, see section 3.1), draw a heatflow-time plot. The heat flow peaks will appear. If a peak meets the end of a zone, the next zone file should be combined to process.

2. Draw baseline with the "Baseline" tool of Origin.

   A baseline segment should meet the start and end point of a peak. The start point is always easy to determine; if the scale of baseline shift is rather small compared with the measured peak, the end point is also easy to determine, or the accuracy of the position of end point will not bring

obvious error to the integral of the following step. However, if a peak signal is not large enough compared with the baseline shift and noises, its end point is not very clear; but the it should be determined as such a point after which the baseline shift is linear.

There are different ways to draw a baseline from the start and the end point of a peak (Höhne et al., 2003), one way is to take the straight line between them.

3. Make the integral of each peak, input the area to the "CALORIMETRY DATA" area of the Excel file.

CALORIMETRY DATA	
Dose #	**Heat Evld / mJ**
1	11,55
2	10,50
3	6,70
4	6,03
5	3,75
6	3,92
7	1,93
8	2,42
9	3,40
10	1,35
11	0,78
12	1,23
13	1,63
14	0,64
15	0,88

After the area of every peak is input, adjust the data series source and the axis scales in the "DIFFERENTIAL HEAT" worksheet of the Excel file, then the differential heat plot will be obtained.

5 In case of Malfunctions and Accidents

5.1 Power switch-off

5.1.1 Before a planned power switch-off

Before a planned power switch-off, the whole setup should be switched off in the following steps:

1. Fill the setup with helium
    1) Close the shut-off valve for CO (7), close the shut-off valve for rough vacuum pump (12).
    2) Close the turbo pump valve (18), open the calorimeter valve (19), open the shut-off valve for helium (8).
    3) Pulse the gas-supplying valve(20) several times then open it, fill the setup with helium (the final pressure depends on the helium pressure controlled by the pressure-reducing valve 6).
    4) Close the shut-off valve for helium (8).

2. Stop the gas-supply and pressure control units
    1) Disconnect the solenoid valve controller (47) and the cable to computer “Quincy”.
    2) Stop the LabVIEW programs in Computer “Quincy” by clicking the round red button in the upper-right of each interface, then close these programs; switch off computer “Quincy”.
    3) Close the gas supply valves, including the valve for helium from central gas supplying system (ZGV), the valve for helium bottle, and the valve for CO. Noting that the valve for CO to be closed is not in “Schrank 5”, it is near the valve for helium from ZGV in the panel (see the second photo of Fig. 2. 11). Be sure not to turn the reducing valves.
    4) Switch off rough vacuum pump (10).
    5) Switch off the turbo pump (13) and the membrane pump (14). They share one switch.
    6) Switch off the PR 4000 (45), voltmeter (46), full-range pressure gauge (16), heater (17), and the power supply for the solenoid valves (48).
    7) Switch off the power for the fans (24).

3. Stop the calorimeter and heating parts
    1) Close the SETSOFT 2000 program, switch off computer “Calvet”.
    2) Switch off the temperature controller 31, 32, 33; switch off the oven for the heated box (28).
    3) Switch off the power of CS 32 controller (40) and the power module for the calorimeter (41) (the latter has two keys and both should be switched off).

4. Switch off the two “NOT AUS” keys on the panel of the Siemens “Sicherungskasten (fuse box)” HT25 on the wall, i.e. the WS220V II 16A S key and T key. They are the keys for this setup.

5.1.2 After the power switch-on

After the power is on, restart the setup in the following steps:

1. Switch on the WS220V II 16A S key and T key on the panel of the Siemens “Sicherungskasten (fuse box)” HT25.

2. Start the calorimeter and heating parts
   1) Switch on the power module for the calorimeter(41), then the power of CS 32 controller (40).
   2) Switch off the temperature controller 31, 32, 33; switch off the oven for the heated box (28). Be sure that the setpoint of the temperature controller for the heating band (32) does not exceed its measured temperature too much (see section 2.2.4).
   3) Switch on computer “Calvet”, start the SETSOFT 2000 program.

3. Start the gas-supply and pressure control units
   1) Switch on the PR 4000 (45), voltmeter (46), full-range pressure gauge (16), heater (17) and the power supply for the solenoid valves (48). Set the temperature of heater (17) as 75°C. Switch on the power for the fans (24) if the heated box is to be heated up.
   2) Open the gas supply valves, including the valve for helium from central gas supplying system (ZGV), the valve for helium bottle, and the valve for CO. Noting if the pressure measured by the gauges do not increase after the valve is open, that means the magnet valve for the ZGV is still closed due to the power switch-off; ask Ms. Astrid Gomann to open it.

      Be sure not to turn the reducing valves.
   3) Switch on the power-failure protector (50), switch on computer “Quincy”, start the two LabVIEW programs (“VENT-PULS” and “M4660A-mV-C3”) in Computer “Quincy”.
   4) Connect the solenoid valve controller (47) and the cable to computer “Quincy”.
   5) Switch on rough vacuum pump (10).
   6) Make sure the turbo pump valve (18) is closed, switch on the turbo pump (13).

5.2 Malfunctions of setup

If any malfunction occurs with the setup, contact with the person in charge according to the malfunction type:

Type	Person in charge	Office	Telephone
Computer hard ware, software and network	Pfeiffer, Heinrich-Josef	NBCF04/662	32-28517
Mechanics, pumps	Otto, Bruno	NBCF04/684	32-24534
Electrics, heating tape, heating elements	Otto, Horst	NBCF04/684	32-24534
Gas supply, safety issues	Buse, Susanna	NBCF04/688	32-26834

If the setup does not work ordinarily, call the persons in the order of the following list:

Order	Person in charge	Office	Telephone
1.	Xia, Xinyu	NBCF 04/692	32-26475
2.	Naumann, Raoul	NBCF 04/692	32-26475
3.	Löffler, Elke	NBCF04/686	32-24102

Their severe phone can be obtained from secretary Ms. Kalender in NBCF 04/690.

5.3 Accidents

This setup uses CO gas, which is severely toxic. If a leakage of CO happens and detected by the alarm system, the gas-alarm will beep. But when it beeps, it is not definitely that the CO leakage comes from this setup. So when the gas-alarm beeps, go to room NBCF 04/664 to see the channel 655-2 (CO in this setup) in the gas-alarm system, and discuss with colleagues to decide whether the CO bottle for this setup should be closed.

If the House-alarm bells, the operator must stop every work at once, switched off the gas, water and air-flow. If possible, switch off plants and equipment. Close the windows and doors (but do not lock them), use the designated escape routes (do not use the lifts), go to the meeting point: parking lot ND, eastern N-Nordstraße. The building may only be entered again with the permission of the officers in charge[8].

For all the procedures in case of danger and fires, read the following website thoroughly:
http://www.techem.ruhr-uni-bochum.de/local/belehrung/verhalten.htm

6 References

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[2] Höhne G. W. H., W. F. Hemminger and H.-J. Flammersheim (2003), *Differential Scanning Calorimetry*. Berlin: Springer.

[3] Spiewak B. E. and J. A. Dumesic (1996), Microcalorimetric measurement of differential heats of adsorption on reactive catalyst surface. *Thermochimica Acta*, Vol. 290, pp. 43-53.

[4] Swagelok Company, http://www.swagelok.com/downloads/webcatalogs/MS-01-140.pdf, Sept. 22, 2004.

[5] Swagelok Company, http://www.swagelok.com/downloads/webcatalogs/MS-01-24.pdf, Sept. 22, 2004.

[6] Caburn Vacuum Science Ltd., http://www.caburn.co.uk/resources/downloads/pdfs/sec1.1.1.pdf, Sept. 22, 2004.

[7] Caburn Vacuum Science Ltd., http://www.caburn.co.uk/resources/downloads/pdfs/sec1.2.1.1.pdf, Sept. 22, 2004.

[8] Laboratory of Technical Chemistry, Ruhr-University Bochum, http://www.techem.ruhr-uni-bochum.de/local/belehrung/verhalten.htm, Sept. 22, 2004.